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A LABORATORY OUTLINE OF GENERAL CHEMISTRY

BY

ALEXANDER SMITH

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PREFACE.

No apology is offered for the preparation of another laboratory manual. Each teacher of chemistry sooner or later catches the infection, and finds himself impelled to prepare an outline of his own. There is little material that is original in the present one. The author therefore acknowledges his indebtedness to other similar outlines. Ramsay's "Experimental Proofs of Chemical Theory," may be named as the source of some of the quantitative experiments.

In selecting, applying, and, to a slight extent, adding to this material, several considerations have been kept in view, although the nature of the case has made it easier to give effect to some of these than to others.

The laboratory work is most emphatically not a mechanical part of the course, in which the use of the intelligence of the student plays no part and all thought is reserved for the home or class-room. It is an essential part of the rigorous study of the subject, requiring the employment of the head as well as the hands. An effort has therefore been made to give continuity to the directions by the form in which they are given, and, by questions, to prepare the way for the correlation of the facts which is accomplished in quiz and lecture. This does not mean that the work forms by itself a complete course of study in the subject. On the contrary, certain important topics, such as Gay-Lussac's "Law of Volumes" with the inferences, based on Avogadro's hypothesis, which may be drawn from it, can more fitly be illustrated in the lectures. The admirable experiments of Hofmann often involve numerous details and precautions in manipulation the need of which the beginner could not have foreseen. The apparatus is difficult to handle on the first trial and its provision involves the teacher of a large class in difficulties. The significant facts to be observed in each case are so very simple as not absolutely to require individual experiment for their comprehension. These facts, however, demand elaborate reasoning for the development of their significance, and anything like spontaneous application by the pupil is very unlikely to occur. Thus the difficulties preceding and following the observation of the central fact render it unsuitable for illustration in the laboratory. On the other hand, when the practical details are subordinated, the diagrammatic nature of these experiments renders them peculiarly adapted for lecture purposes, for which, in fact, they were originally designed. Then, too, the measurement of volume appeals to the eye more directly than the measurement of weight and is, therefore, more suitable for the lecture room. The measurement of weight, on the other hand, is most convincing when carried out by the pupil himself and is, therefore, better adapted to form the basis of the majority of the quantitative laboratory experiments.

Many other cases of the omission of familiar experiments, with a view to their utilization in the lecture, will be noted.

The science of chemistry deals with natural phenomena themselves, and not what various authors have said about them. It is the part which the pupil can learn first-hand in the laboratory by observation and inference, and not the part, indispensable though it is, which he borrows from the book or teacher which will correctly shape his attitude toward the whole science. Much opportunity for induction has therefore been provided. This aspect of the work has been emphasized by an effort to discredit reliance on books. For this purpose experiments with easily ascertainable results, whose course nevertheless cannot be anticipated by reference to the usual run of text-books, have been introduced occasionally. Such are the action of concentrated sulphuric acid on ferrous sulphide (p. 47), and of magnesium on nitric acid (p. 60).

There is an absurdity inherent in the usual course of directing a pupil to make a single qualitative experiment, with haphazard proportions of the materials and other conditions largely selected by chance, and then asking him to write an equation, that is, to draw a quantitative conclusion. The pupil feels this distinctly, although he may attribute it to the wrong cause. He usually lays it to the lack of certainty in the conclusions of the science rather than the defect in the method of teaching it. This discrepancy between the meager extent of the data and the precision of the quasi-conclusion is, perhaps, as a rule, unavoidable, since quantitative investigation of all the chemical changes studied is impracticable. Experiments like the burning of phosphorus in oxygen, in which the pupil's notes may run: "Saw white fumes; concluded that the product was a white solid of the composition P_2O_5," are bound to form a large part of the course.

We must, however, remove the possibility of the student's thinking that induction in chemistry is mainly a pretense of reasoning. The debt to the exact investigation to which the action can be subjected, and to the reference book containing the results of this, should be acknowledged. It is clearly indispensable also that in a few cases the whole distance should be bridged. This may be done partly in the lecture room and partly in the laboratory. In this way the pupil will learn that although the combining proportions are not usually measured they are always definite and measurable, and he will follow, in a few cases at least, the whole course of the experiment from the qualitative external characteristics to the final construction of the formulæ and equation. It is not always convenient to follow quantitatively every feature even in one of these selected chemical changes, but some features may be investigated closely in one, and others in another, with a resulting synthesis of the whole process in the mind of the pupil. Thus in the burning of phosphorus the composition of the pentoxide cannot be measured by the beginner. Again, in the determination of the combining weight of zinc with oxygen (p. 18), the action of the nitric acid on the zinc and the effect of heating the nitrate are passed over to avoid premature discussion of the properties of nitric acid. The action of carbon on oxygen (pp. 10 and 12) is an example of the more complete investigation of a chemical change.

Even in cases where the quantitative aspect is deliberately left to be supplied by the book, there are often essential factors in the material from which a conclusion is to be drawn which are, at the time, unknown to the student and beyond his observation. Where these occur a direct reference to the text-book is enjoined by inserting an R in parentheses in the directions. Thus in Chap. IV (Oxygen), 3 and 4, the interaction of certain anhydrides with water, the solubilities of nitrates, chlorides and chlorates of potassium and silver, etc., are involved in the understanding of the chemical changes observed. This sign is intended to enable the pupil to distinguish when he is expected to rely on himself and when he must seek aid, while being held responsible for reaching the correct conclusion in either case. To carry out this idea, as well as on other grounds, a few volumes for reference (including a table of solubilities) should be provided in the laboratory.

Experiments have been inserted to illustrate such theoretical matters as the measurement of the strength of acids and phenomena of chemical equilibrium, ionic equilibrium, solution tension, etc, since these ideas cannot be grasped in such a way as ever to be applied unless they are interwoven with the facts they explain. Their introduction requires no justification. Physical chemistry cannot be taught in the first year of general chemistry, but its results are absolutely indispensable to a rational correlation and explanation of the facts dealt with in general chemistry.

In Chaps. I – IX, which form one third of the year's work, the lectures precede the laboratory work, while not covering altogether the same ground. In this way the beginner acquires some knowledge of the nature of the substances he is to handle, and of the sort of results he is to look for. In Chaps. X – XXIV, the lectures follow the laboratory work and the latter is therefore more strictly inductive than in the earlier chapters.

The work outlined is designed to occupy about six hours of laboratory work per week for nine months, on the assumption that a small proportion of the experiments is selected for omission or transference to the lecture room. The order in which the elements are presented and the period at which quantitative work is introduced may readily be changed as circumstances demand.

College students who have already completed a year of chemistry in a secondary school will naturally have performed many of the experiments here given, and have learned all they can teach. A selection, by way of suggesting a basis for a college course in continuation of school work for such students, is printed in the appendix.

The outline of laboratory study presented here has been used in proof with five classes in this university and defective parts have been altered until a workable form has been reached. In this way every paragraph has been rewritten or amended.

I have to thank Professor J. B. Garner (Bradley Institute), and Dr. H. N. McCoy (of this laboratory) for many valuable suggestions. I owe to the latter also the admirable working out of the details of the quantitative experiments on the composition of Carbon Dioxide (p. 12), on the proportions of copper to oxygen in the two oxides (p. 17), on the combining weight of zinc (p. 18), and on the estimation of the activity of an acid (p. 39), as well as the realistic arrangement for making sulphuric acid from pyrite (p. 49). Finally I have to express my indebtedness to Miss Carol Paddock for preparing the illustrations.

Chicago, May 1899. ALEXANDER SMITH.

CONTENTS.

GENERAL INSTRUCTIONS.

Check your apparatus by comparison with list, have deficiencies made good at the storeroom, obtain the key of a locker in the hall, enter the numbers of this and the desk keys on the list, and then sign and return the list to the storekeeper.

Read the "Regulations" posted in the laboratory.

Provide yourself with a **notebook** and make a careful permanent record immediately after each experiment. Enter the numbers of the chapters and paragraphs of the outline systematically, so as to save the necessity of copying the directions, and place the same numbers at the head of each page in the notebook. State 1) what you did, if anything beyond the directions, 2) what you observed, 3) what conclusions you drew. A sketch of the apparatus will enable you to recall the circumstances of the experiment, if later reference to it is necessary.

Wherever an **interrogation point** (?) or a direct **question** appears, a corresponding note should appear in the notebook.

The very numerous **questions** asked in the course of this outline are intended to be answered, not by speculation, but by careful observation, and reasoning based on the results of this. In many cases the student will find it necessary to devise and carry out further experiments of his own before a satisfactory answer is obtained. In some more complex cases, where much time and work would be necessary, the books set apart for reference are to be consulted. An [R] indicates such necessity. This should be done, however, only after the experiments have been made and the notes written up as far as possible.

The equation should always appear when a chemical change has been observed, but an equation alone is never a sufficient record.

Where the word [Instructions] appears, consult the instructor before going further.

In experiments marked [Quant.] use the finer balance, in all other cases the rough scales in the laboratory.

The expression [Temp. order] indicates that the necessary apparatus must be obtained from the storeroom on a temporary order.

Where exact quantities are not indicated, very small amounts of solutions (1 c.c. or less) should be taken. This advice is given, partly to secure saving of material, but chiefly to avoid the waste of time which working with large quantities always entails.

All students must work independently except where coöperation of two students is expressly directed.

CHAPTER I.

APPARATUS.

1. INSTRUCTIONS.

a. Read the general instructions preceding this chapter very carefully, and do not fail to observe them.

b. The number of blast-lamps and balances being limited, the whole class cannot perform the experiments in this chapter simultaneously in the order given. Two students from the group under each assistant, as soon as they have checked their list of apparatus and completed **2**, will be sent to the blast-lamp table to carry out 3 under the direction of a special assistant. Two others, after completing **2**, will pass to **5** and **6**, returning to **4** when these are accomplished. The remainder of each section will be sent as early as possible in pairs to take the places of those returning from glass-blowing (3) and weighing (6), and meanwhile will occupy themselves with 4 and 5, or work in Chap. III.

c. Chap. II is intended for those only whose preparation in physics is defective. It is therefore to be omitted, except in cases where personal instructions to the contrary are given.

2. CONSTRUCTION OF A WASH BOTTLE. Select a good cork and soften it by means of the cork press. Bore two holes with a cork borer and smooth them with a file. Prepare two glass tubes as in Fig. 1 (see note on bending under 3, *d* below), round their edges and insert them. Make the nozzle by softening a piece of tubing in the flame, drawing it to capillary dimensions and cutting. Connect it by means of a short piece of rubber tubing [Storeroom]. Test the apparatus to see that the joints are air-tight [Instructions]. Fill the bottle with distilled water. (Distilled water is used for nearly all experiments and for rinsing glassware.)

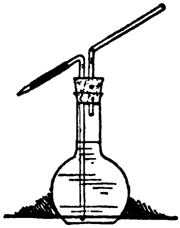

FIG. 1

3. GLASS BLOWING [Instructions and notes below].

a. Cut a small piece off the wide glass tubing.

b. Make a test-tube of soft glass.

c. Make a test-tube of hard glass.

d. Connect two pieces of narrow glass tubing to make a longer piece.

NOTES.—Always round off the edges by softening in the Bunsen flame. In the case of test-tubes, use a pointed piece of charcoal or a file for spreading the mouth. Always distend softened parts by blowing and then cover with soot in the luminous flame before allowing finally to cool, otherwise cracks will appear.

In bending glass tubes, always use an ordinary flat luminous flame. Never employ the Bunsen flame. Discover the reason for this injunction by bending a tube in the Bunsen flame and comparing the result with a bend made in the proper way (?).

4. BUNSEN BURNER.

a. Notice the effect of opening and closing the holes at the bottom of the tube. What is the proximate cause of the difference in the flames?

b. Notice the structure of each flame. Determine which parts are relatively hotter and which cooler, by placing a match and a piece of platinum wire across the flame in various parts and by causing the flame to impinge on a sheet of paper spread flat on the table. Make sketches showing the real form of the flame. Where would you hold an object in the non-luminous flame in order to get the greatest heating effect? Which region will be deficient in oxygen and which will have excess? Name those regions.

c. Fuse the end of a piece of glass rod (75 mm. long) in the blast lamp and insert a short piece of platinum wire [Storeroom]. Make a bead of borax on the straight wire, using the non-luminous flame. Observe the behavior of the borax and explain [R]. The bead must be small to avoid its dropping off.

d. Dissolve a speck of manganese dioxide in the bead by heating in the oxidizing flame and observe the color of the bead.

e. Heat this bead in the reducing flame [Instructions].

f. In the oxidizing flame again.

5. MEASURING VESSELS.

a. Fit a burette with a short piece of rubber tubing and nozzle. The exit may be closed either by means of a pinch clamp or by placing a small piece of glass rod in the middle of the rubber tube [Instructions].

b. Fill the burette with distilled water, taking care that the air below the clamp is completely expelled. Read the height of the water in the burette, observing the lower side of the meniscus and estimating tenths of a division.

Measure 10 c.c. of distilled water into each of two test-tubes, the first with a graduated cylinder, the other with the burette. Sketch one test-tube with contents full size.

c. Measure by means of the cylinder the volumes of water your flasks and beakers hold, and record the figures.

6. USE OF THE SIMPLE BALANCE [Instructions; Quant.].

a. Allow the beam of the balance to swing and observe whether the pointer makes equal excursions on each side of the zero point. If it does not, correct the defect by placing small pieces of paper in one pan. In weighing any object, weights are added in the other pan until the vibrations of the pointer on each side are equal (not by bringing the beam to rest!).

Place a 10 gr. weight in each pan, equalize the vibrations as above, add the .01 gr. weight to the right-hand pan and find the reading about which the pointer now oscillates. This gives the deflection for .01 gr. and may be used for estimating weights less than .01 gr.

NOTES.—Great care must be taken not to injure the balance or the weights. The pans of the former must be let down every time weights or other objects are added or removed. Objects to be placed on the pans must be carefully cleaned and dried. Solids to be weighed must be placed on a piece of glazed paper, or a watch glass, never on the pan directly. The weights must be lifted by means of the forceps, not by the hand. If the weights are touched by the hand, they oxidize rapidly and become inexact. In reckoning, count first by the places vacant in the box and check by counting the weights themselves. This will enable you to avoid the commonest error in weighing.

b. Ascertain the weight of a small dry beaker. Measure into it a quantity of water (about 10 c.c.) from the burette and weigh again [See note below].

Repeat any one of the readings of the burette several times, without referring to the notes of the previous readings, and record the results. From these estimate the error of such readings in hundredths of a c.c. and express it in per cent. of the volume being measured when the reading was made.

NOTE.—Wherever in this outline instructions like the above are given, do not attempt to take the exact amount specified, but ascertain exactly how much has been taken. A quantity is indicated because one approximating that named will be most convenient for the apparatus and for securing the object in view.

CHAPTER II.

PHYSICAL PROPERTIES.

1. SPECIFIC GRAVITY [Quant.].

a. Calculate from the above result (Chap. I, 6, *b*) the specific gravity of water (weight of 1 c.c.). Criticise the result. Repeat the measurement and calculation with the solution of sodium carbonate on your desk, and with chloroform. Dry the burette before filling with chloroform. Be careful not to let these or any liquids reach the pan of the balance.

b. Suspend a piece of thread from the hook above the pan of the balance and bring the pointer to zero. Tie to this thread a short piece of thick glass rod and weigh first in air, then in water. Calculate the specific gravity of glass.

NOTE.—Use the shelf of your pneumatic trough as a bridge over the pan on which to support the beaker of water.

c. Make a mark with your file in the middle of the neck of a flask holding about 25 c.c., fill with distilled water to the mark and weigh. Weigh some small pieces of sulphur (about 2 gr.), put them into the flask, bring the level of the water to the mark again, and weigh once more. Calculate the specific gravity of sulphur.

2. CHARLES' LAW [Quant.].

Take a dry flask [Instructions] of 300 c.c. capacity and fit it with a rubber stopper, short pieces of glass and rubber tubing, and clip as in Fig. 2. Find the weight of the flask as thus fitted (w). Make a mark on the neck of the flask at the bottom of the stopper and always insert the latter the same distance. Place the flask vertically in a pot of boiling water so that it is immersed completely, holding it in position by means of a universal clamp, and open the clip. After several minutes close the clip, remove the flask, invert it in a pneumatic trough filled with water, open the clip to allow the water to enter, equalize the level inside and out, close the clip, dry the outside of the flask carefully and weigh (a). Fill the flask and tube completely with water and weigh again (b). Take the temperature of the water in the trough (t), and of the boiling water (t_1).

FIG. 2

Subtracting the weight of the flask (w) from (a) gives the volume of water which entered (1 gr. = 1 c.c.). Subtracting the weight of the flask from (b) gives the total volume of the flask Subtracting these two differences, we get the volume of air which partially filled the flask at t°, and completely at t_1°. The difference between t° and t_1° gives the change in temperature. Calculate the expansion (in c.c.) of 1 c.c. heated from t° to $t° + 1°$. Express this as a common fraction. What is the theoretical result calculated from Charles' law?

The result is the same whatever gas or mixture of gases is taken. (Exceptions, R?)

3. BOYLE'S LAW [Quant.].

Take a T tube (Temp. order) and connect one of the short arms with the apparatus used in last experiment. (The flask must be dry as before.) Close the other short limb with a piece of rubber tubing and another clip. Immerse the long (40 cm.) limb in a beaker of mercury. Open both clips and exhaust the air as far as possible by sucking. Close the clips and measure the height of the mercury in the tube. Disconnect the T tube, leaving the clip on the flask closed. Open this under water, equalize the levels, close the clip and weigh. Ascertain the height of the barometer (p).

Subtracting the weight of the flask (known) from the above weight gives the volume of water which entered. Subtracting this volume from the known total volume (d), we get the volume (c) of the air which partially filled the flask at atmospheric pressure (p) and completely at the reduced pressure (p′). Get (p′) by subtracting the height of the mercury from (p).

Boyle's law states that c:d::p′:p. Calculate (d) from (c), (p′) and (p) by this formula and compare with the value of (d) observed.

CHAPTER III.

CHARACTERISTICS OF CHEMICAL CHANGE.

1. QUALITATIVE STUDY OF CHEMICAL CHANGE.

a. Fit up an aspirator, attach to it a piece of hard glass tubing 20 cm. long, close the other extremity of this with a stopper fitted with glass tube, rubber tube and clamp, and provide the other tubes and beaker all as shown in Fig. 3. The stopper of the aspirator should be of rubber. Test the apparatus and see that it is perfectly air-tight before proceeding further. Weigh out roughly into a

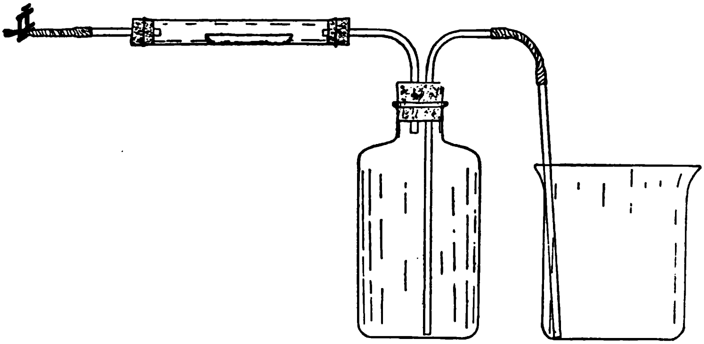

FIG. 3

porcelain boat about 1 gr. of powdered iron, which should be dried previously by heating it gently in a test-tube. Examine the physical properties of the iron and note the results. Place the boat in the middle of the tube. Fill the aspirator to the neck with water and put the tubes in position, without, however, finally inserting the stopper. Displace the air in the hard glass tube with a gentle stream of oxygen from the cylinder of compressed oxygen, and then press the stopper home and pass in more oxygen until most of the water has been driven over into the large beaker placed to receive it. The level of the water should not fall below that of the lower end of the long tube of the aspirator. Close the spring clamp behind the hard glass tube. The object of this operation is to expel nearly all the air and to fill the apparatus with a volume of confined oxygen. Any subsequent change in this volume of oxygen will be accompanied by the entrance or exit of water through the rubber tube and nozzle. To record the amount of oxygen at starting, leave the overflow beaker full of water, lower it until the levels of the water in the bottle and beaker are the same (why?), and paste a small strip of paper on the outside of the bottle to mark the height of the water. Now heat the iron, at first gently, and then strongly (see note) with the bunsen flame, noticing all that happens. If the volume of the oxygen changes, continue the operation till no further change occurs. Finally, when the tube has cooled, mark the level of the water again in the same manner as before and then weigh the boat and contents and examine the latter. Which of the characteristics of chemical change were observable?

NOTE.—A piece of wire gauze bent in cylindrical form and placed round the part of the hard glass tube which is to be heated will diminish the risk of cracking and should be used in this and all subsequent experiments of the same nature.

b. Gunpowder is made from nitre (potassium nitrate), roll sulphur and charcoal. Bring specimens of these substances from the side-shelf on watch glasses, and examine them as regards properties which could be used for separation and recognition. The solubility of each in water and carbon disulphide will be most useful for the former. Examine some gunpowder, from the side-shelf. Does it resemble the constituents physically? Devise a method of ascertaining whether it is still a mixture of these substances, or has changed chemically during manufacture. Try your method(?).

NOTES.—Pour away all ill smelling substances, like carbon disulphide in the sink in the hood, and not in the ordinary sinks or jars.

In filtering, always cut the paper to circular form with scissors and, to avoid loss of any of the liquid, use as small a paper and funnel as will serve the purpose. Never allow the paper to project above the edge of the funnel. It should not come within less than one-quarter of an inch of the top of the latter (*cf.* Fig. 9).

2. LAW OF DEFINITE PROPORTIONS [Quant. *cf.* Chap. I, **6**, *b*, note].

a. Prepare two burettes and two evaporating dishes. Weigh an evaporating dish. Dilute 25 c.c. of strong hydrochloric acid with an equal volume of water, and fill a burette with it. Fill the second burette with ammonium hydroxide solution. From the first burette run 5 c.c. of the acid into the dish and add a drop or two of litmus. Read the burette containing the ammonium hydroxide and run the solution into the acid, drop by drop (stirring constantly), until the exact point is reached at which the litmus becomes blue. Evaporate [Hood] the solution to complete dryness on the steam bath, cool and find the weight of the ammonium chloride produced.

Weigh the second evaporating dish, take 5 c.c. of hydrochloric acid as before and add twice the volume of ammonium hydroxide used in the previous experiment. Evaporate [Hood] and weigh as before.

Compare the amounts of ammonium chloride found in the two experiments and interpret the result.

b. Carefully weigh an evaporating dish and weigh out into it about one gram of crystallized sodium carbonate. Dissolve in dilute hydrochloric acid, adding little by little and covering with a watch glass between successive additions to avoid loss by spirting. When the solid has wholly dissolved, wash the watch glass over the dish, and evaporate [Hood] the contents of the latter on the steam

bath. Allow the dish to cool and weigh. Calculate the ratio by weight of the carbonate taken, to the salt produced, 1 : x.

A small flask is very convenient for the action of the acid on the carbonate, and the contents can afterwards be rinsed into an evaporating dish.

Repeat the experiment, using about two grams of the carbonate, and find the ratio. Compare the ratios and interpret.

CHAPTER IV.

OXYGEN.

1. SOURCES. Heat small quantities of barium peroxide, lead dioxide, potassium bichromate and manganese dioxide separately in a hard glass test-tube, observe whether any gas is given off and apply the test of the glowing splinter of wood. If the Bunsen flame proves inadquate, try the blast-lamp. Describe the residues.

NOTE.—Commercial manganese dioxide sometimes contains charcoal and it is therefore dangerous to use it for mixing with potassium chlorate in making oxygen without first heating a little alone. Signs of glowing indicate the presence of a combustible substance.

2. PREPARATION. Mix on paper about 3 gr. each of potassium chlorate and powdered manganese dioxide. Put the mixture in a hard glass test-tube closed with a cork and fitted with a piece of glass tubing and a rubber delivery tube. Heat carefully, so as not to cause too violent an evolution of gas, and collect in four bottles over water. Remove the delivery tube from the water as soon as the bottles are full (why ?). [Advanced students: Weigh with care [Quant.] the manganese dioxide employed, drive all the oxygen off without collecting it, and set the tube aside for use in 4, *a*.]

3. PROPERTIES.

a. Lower a little ignited sulphur in a deflagrating spoon into one bottle (?). Remove the spoon, add a little water, close with the hand and shake (?). Test the water with litmus [R].

b. Lower a very small piece of burning phosphorus into the second bottle in the same way (?). [Instructions: Phosphorus must always be cut under water and handled with forceps. Great care must be taken not to touch it with the hand, as it catches fire easily and causes very severe burns. Red phosphorus is safer and should be substituted here if available.]

Proceed as in *a* (?). Test with litmus [R].

c. Lower a piece of glowing charcoal into the third bottle (?). Treat as before (?). Test with lime water [R].

4. CHEMICAL ACTIONS INVOLVED IN THE PREPARATION OF OXYGEN [Advanced students].

a. Devise a way of separating the substances left in the tube used in 2 and of ascertaining whether the manganese dioxide has been altered. Recover the potassium chloride and compare its appearance with that of the chlorate. Test solutions of each with silver nitrate and explain the result [R].

b. Behavior of potassium chlorate alone: preparation of perchlorate [Quant.].

Measure 500 c.c. of water into your 1 liter bottle, and mark the level reached. Observe the temperature and pressure of the air and calculate the weight of potassium chlorate which will be necessary to give this volume of oxygen while leaving the perchlorate and chloride behind [R]. Weigh this quantity of chlorate into a rather wide hard glass test-tube fitted with a cork and delivery tube. See that the apparatus is air-tight [Instructions]. Heat the chlorate and drive off enough gas to fill the bottle by displacement to the mark. Proceed slowly towards the end so as to allow the gas to cool, stop heating when the mark is reached and remove the tube at once from the water. Pour the melted substance into a mortar before it has time to solidify. Powder the mixture, boil with 20 c.c. of water and let the solution cool. Pour the liquid away from the crystals (what will the solution contain ? R) and dissolve them by heating with 20 c.c. of water once more. Allow the solution to stand for an hour or two and filter off the crystals. (Use a small filter paper just large enough to hold them.) Wash them with a little distilled water as they lie on the filter and dry on a radiator, Dissolve a little of the substance in distilled water and test with

silver nitrate solution (why?). Explain the principle underlying this process of purification.

5. SLOW OXIDATION OF METALS. Devise a way of showing that moist iron filings absorb oxygen from the air when they rust, and try it.

6. WEIGHT OF A LITER OF OXYGEN, USING ASPIRATOR. [Quant.].

a. Powder some potassium chlorate, and dry it on a watch glass on the radiator or steam bath. Construct an aspirator (Fig. 4), using the 1 liter bottle, and connect it with a hard glass test-tube. Fit a nozzle to the rubber tube. Test the apparatus to see that all the joints are air-tight [Instructions]. Fill the bottle with water so that the short tube is not immersed. Fill the rubber tube and nozzle with water and close the clamp. Weigh the hard glass tube, put into it about 1 gr. of the chlorate, weigh again and connect with the bottle. Allow the rubber tube to hang to the bottom of a beaker (300 c.c.) containing some water. Open the clamp and raise the beaker till the levels of the water in this and the bottle are the same, and the gaseous pressure therefore alike in both. Close the clamp again, empty the beaker and replace it.

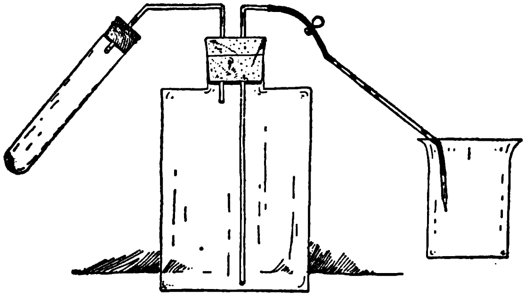

FIG. 4

Open the clamp once more and decompose the salt slowly by heating, catching in the beaker the water driven over by the gas. Stop heating if the tube shows signs of softening, or when the decomposition is complete. Allow the whole apparatus to stand until it has reached the temperature of the air. Equalize the level of the water in both vessels and close the clamp.

Measure the volume of water in the beaker. It will be equal to that of the gas evolved (what of the air originally in the apparatus?). Weigh the tube once more and observe the temperature and pressure of the air.

Subtract the aqueous tension at the observed temperature (see appendix) from the barometric reading to get the true (partial) pressure of oxygen in the bottle. Reduce the volume to 0° and 760 mm. Subtracting the weight of the salt remaining from that of the chlorate gives the weight of this volume of oxygen. Calculate the weight of 1 liter and the volume of 32 gr.

Test aqueous solutions of the chloride and chlorate with silver nitrate solution and explain the result [R].

To what class of gases would the use of the aspirator be confined for purposes like the above?

b. If the condition of the hard glass tube from **6,** *a* will permit, detach and heat it with its contents once more to drive out the last traces of oxygen. Allow it to cool and weigh it. Obtain the weights of chloride and total oxygen by difference.

Calculate the ratio of the weight of potassium chloride to that of oxygen ($1 : x$) and, given the formula of the former (KCl) and its formula weight, 74.5, and that of oxygen, 16, determine the formula of the chlorate. Show how this gives the equation.

7. COMPOSITION OF CARBON DIOXIDE [Quant.].

NOTE.—Two students may with advantage carry out this experiment together.

Fit a piece of hard glass tubing with perforated corks and insert at one end a short piece of glass tubing and at the other a U tube, as in Fig. 5. Attach to the U tube by means of a cork a short straight tube, of the diameter of a test-tube, which has been drawn out so as to leave a small opening at the free end. Arrange a loop of wire with which to suspend the potash tubes from the balance. Place in the hard glass tube a plug of granular cupric oxide, or an

oxidized spiral of copper gauze, about 5 cm. in length. The former may be held in position by small wads of asbestos. Put about 0.2 gr. of pure dry sugar-charcoal in a porcelain boat, weigh the boat with contents, and set it in the tube close behind the cupric oxide. Make a few c.c. of a strong (approximately 30 per cent.) solution of potassium hydroxide, fill the bend of the U tube with it, and charge the small tube beyond with fragments of solid caustic potash. Test the apparatus to see that it is air-tight. Finally, weigh the connected potash tubes immediately before starting the combustion.

Slip the cylinder of wire gauze over the hard glass tube, connect the latter with the oxygen cylinder (or other source of oxygen), and heat the part containing the boat and cupric oxide with two burners. Turn on the oxygen with care and regulate the stream so that the carbon may burn slowly and not more than 15–20 bubbles of unused oxygen escape per minute. A more rapid stream will involve the loss of carbon dioxide. Heat the front of the boat first and let the glow, caused by the combustion, travel along. The burning will take 30–45 minutes. Continue the stream of oxygen for 4–5 minutes after the carbon is completely burned (why?), then disconnect the potash apparatus and weigh it. A more accurate result is obtained by displacing the oxygen by air (why ?). After the tube has cooled, weigh the boat with any ash it may contain. Return the cupric oxide to the bottle.

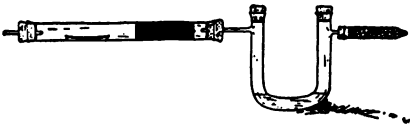

FIG. 5

The loss in weight of the boat gives the amount of carbon ; the gain in weight of the potash apparatus, the amount of carbon dioxide. The difference of these two gives the oxygen. Calculate the percentage composition of carbon dioxide and the ratio of carbon to oxygen, assuming the weight of the latter to be 16. Assuming the atomic weights of carbon and oxygen to be 12 and 16 respectively, deduce the formula of carbon dioxide from your experiment. How does this result give us the equation ?

CHAPTER V.

HYDROGEN.

1. INTERACTION OF METALS AND ACIDS.

a. Place a small piece of each of the metals, tin, copper, iron, zinc, lead, aluminium, and magnesium with a little pure [Side-shelf] concentrated hydrochloric acid in a test-tube. Observe each case critically, and record the results. Note the effect of heating, if no action occurs in the cold. After the action has ceased, evaporate [Hood] any one of the solutions to dryness on the sand bath (?).

b. Try in the same way the action of dilute sulphuric acid on copper, zinc, and iron. In case little or no action takes place in the cold, try the effect of putting a platinum wire in contact with the metal (?) and, having withdrawn the wire, of adding a drop of cupric sulphate solution (?) before resorting to heating. If any effect is observed, notice where the hydrogen appears to come from, and explain [R]. Filter the solution of the last metal, concentrate on the steam bath, and set it aside to crystallize [Instructions and notes below].

NOTES.—If the solution has been sufficiently concentrated, and yet crystals fail to appear in twenty-four hours, a clue to the fault may be obtained by evaporating some dilute sulphuric acid alone on the steam bath, adding a crystal of ferrous sulphate when it has cooled, and observing the fate of the crystal.

Notice that "evaporating to dryness" does not usually give crystals. To get good crystals the antecedent "concentrating" must be accomplished with great care and skill.

c. Try the action of dilute acetic acid on iron.

d. For comparison, study the action of concentrated sulphuric acid on zinc in the cold and in the heat.

2. INTERACTION OF METALS AND WATER.

a. Recall the action of sodium and potassium on water [Lecture].

b. [Two students working together.] Place about 20 cm. of magnesium ribbon in the higher end of an inclined hard glass tube, fitted with two perforated corks. In the same end insert

a delivery tube. Fit a flask like that used in generating hydrogen (Fig. 6), and heat some water in it until a regular stream of steam issues. If the stream is unsteady, put some broken porcelain into the flask. Now heat the magnesium with another burner, connect the flask so as to pass steam over the heated metal, and collect the resulting gas over water in a cylinder. When enough has been collected, or the magnesium is all oxidized, remove the delivery tube from the water, and apply a light to the gas in the cylinder.

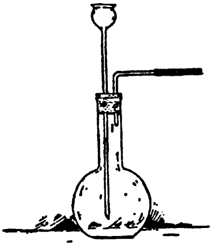

FIG. 6

c. The sodium hydroxide formed from water in *a* may undergo further change by heating with a fresh quantity of sodium. It is more convenient to use another metal for the purpose, however.

Prepare a hard glass test-tube and a delivery tube. Rapidly powder some sodium hydroxide (1 part), mix it with zinc-dust (1 ½ parts), heat in the tube and collect the gas over water. Ascertain whether the gas is combustible. What information about water do the results of *a* and *c* together give us? What is the solid product [R]?

d. Place about 5 gr. of zinc-dust in a test-tube and shake, for a few seconds only, with a dilute solution of cupric sulphate (?). Pour off the solution and wash the zinc once with distilled water by decantation. Take special care not to shake with air during the washing as the metals are easily oxidized and their action impaired. Finally cover the zinc with water, fit the test-tube with a cork and delivery tube, and boil. Collect the gas over water and determine whether it is combustible. Make a general statement about zinc on the basis of 1, *a* and *b*, and 2, *d:* also about the hydrogen in water and acids.

3. PREPARATION OF HYDROGEN [Same apparatus for 4 and 5].

a. Put some zinc in a flask (Fig. 6) provided with a rubber delivery tube, add diluted hydrochloric acid and test the issuing gas till it is found free from air. (It must not be ignited at once, or the apparatus may be blown up. Samples must be caught in test-tubes till they are found to burn quietly.)

Ascertain whether ordinary combustibles burn in the gas. Show whether it is lighter or heavier than air. Fill a test-tube with one-third hydrogen and two-thirds air and apply a light to the mixture.

4. PRODUCT OF THE UNION OF HYDROGEN AND OXYGEN. Attach a glass tube drawn out to a capillary opening in place of the delivery tube. Ascertain that the issuing gas is not explosive (test ?). Hold a cold dry beaker against the jet of unlighted gas. If moisture is deposited (what is its source ?), insert a U tube filled with chloride of calcium to dry the gas. When the gas no longer deposits moisture, set fire to it and hold the beaker over the flame (?).

Burn ordinary illuminating gas from the same nozzle and hold the beaker over the flame (?).

5. REDUCTION.

a. [Two students working together.] Arrange a hard glass tube, like that in Fig. 5, fitted with perforated corks and short tubes. Place aluminium oxide, ferric oxide, and minium, successively in the tube. Dry each oxide by heating in a porcelain crucible before use. Connect with an apparatus delivering dry hydrogen and heat the oxide in a slow stream of the gas. After each time the apparatus has been opened, wait till all the air has been displaced by hydrogen before heating (why ? test ?). Observe the effect on each oxide and whether water condenses in the tube.

Ascertain the common names of the oxides used [R]. Of what chemical change shown in the lecture room is the action on ferric oxide a reversal ? [Advanced students : How does this illustrate mass action ? R.]

b. Mix thoroughly equal bulks of magnesium powder and powdered calcium carbonate, put the mixture in a test-tube (it should fill about half an inch of the tube), and heat the top layer in the Bunsen flame until the reaction begins. It will go on to completion by itself. Be careful to keep the tube directed away from the face during the heating. Allow the test-tube to cool, add a little water,

and then, slowly, an excess of dilute hydrochloric acid (?). When all action has ceased, filter and wash the black residue (?) with water. After drying this on the radiator or steam bath, prove that it is carbon. This may be done by placing some of it in a dry test-tube, leading in a little oxygen from the cylinder, heating in the Bunsen flame and pouring the gas over into a test-tube containing lime water (Chap. IV, 3, *c*). What is the reducing agent in this action ?

CHAPTER VI.

LAWS OF CHEMICAL COMBINATION.

1. MULTIPLE PROPORTIONS [Quant.].

a. Fit a hard glass tube 25 cm. long with corks, through which pass short pieces of narrow glass tubing. To one of these connect a Kipp's apparatus for generating hydrogen and a gas washing bottle (shown in Fig. 8) one-half full of concentrated sulphuric acid. Make sure that the apparatus is air-tight. Dry some powdered cupric oxide by heating it in a hard glass test-tube. Dry also some cuprous oxide (it must be specially prepared for this experiment by precipitation) *in vacuo.* This substance is more difficult to dry than the other, and must be heated strongly in a hard glass test-tube connected with a water pump [Obtain the pump, safety bottle, and connecting tube with rubber stopper on temp. order]. Weigh a clean, dry porcelain boat for each oxide, and place in each about 1 gr. of the proper oxide and weigh again. Be careful in recording the weights and in handling the boats to distinguish the one from the other. Place the boats in the hard glass tube, that containing cupric oxide in front, and surround it with a piece of wire gauze.

Pass a gentle stream of gas through the apparatus until a test (?) shows that the air has all been displaced. Now heat the boats moderately, beginning with the front one. What collects in the rear of the boat ? Where does it come from ? When the action, which requires 10–15 minutes, is finished, allow the boats to cool in a stream of hydrogen. Weigh the boats and contents (?), taking care not to interchange them.

Assuming the combining weight of oxygen to be 16, calculate, from your results, that of copper in each oxide. What is the ratio of the two values for copper? To what formulæ for the two oxides do your results lead, and to what equations?

b. If the experiment in Chap. IV, **6**, *b*, was carried out, dried potassium perchlorate may be decomposed in the same way and the results compared. Simply use an open, long, hard glass test-tube, without aspirator, and drive off the oxygen slowly. Calculate the weight of potassium chloride remaining to that of oxygen ($1 : x'$). Given the formula weight of the former (74.5), and assuming the combining weight of oxygen (16), determine the formula of potassium perchlorate.

2. COMBINING WEIGHTS [Quant.]. The combining weight of metals such as zinc and copper with oxygen may be found by converting a known weight of the metal into nitrate by the action of nitric acid and obtaining the oxide by ignition of this salt.

Weigh a small evaporating dish, place in it about 0.5 gr. of pure zinc and weigh again. Cover the dish with a watch glass, convex side downwards, and add 5 c.c. of water and then pure [Side-shelf] concentrated nitric acid, a few drops at a time, so as to maintain brisk but not violent action. After the zinc is completely dissolved, rinse the cover glass carefully into the porcelain dish and allow the solution to evaporate as far as possible on the steam bath [Hood]. Then, holding the dish with a clean pair of crucible tongs, evaporate the remaining syrup-like solution high over a Bunsen flame, taking the greatest care to avoid any loss of the substance by spirting. When the residue (?) is dry, heat it to redness for a few minutes. Allow the dish and contents (?) to cool and weigh them. Assuming the combining weight of oxygen is 16, calculate that of zinc in zinc oxide.

NOTE.—To make sure that the decomposition was complete, heat once more, cool and weigh again. This precaution is always necessary in experiments of this nature.

3. EQUIVALENT OF A METAL BY DISPLACING HYDROGEN [Quant.].

a. First fill the pneumatic trough and 1 liter bottle with water so that the latter may acquire the temperature of the room. Boil about half a liter of water and allow it to cool. Fit a 100 c.c. flask somewhat as in Fig. 6, using, in place of the thistle tube, a dropping funnel. The stem of the latter must reach to the bottom of the flask, and the inner end of the other tube must be flush with the bottom of the cork. Attach a rubber or glass delivery tube and see that the apparatus is air-tight. Weigh a piece of chemically pure zinc, taking about 2 gr. Without detaching your platinum wire from the glass rod, wrap it tightly round the zinc (why?), and allow the whole to slide gently into the flask. Fill the apparatus by pouring part of the boiled water through the funnel, leaving the bulb of the latter alone empty, and close the stop-cock. Invert the 1-liter bottle, filled with water, on the shelf of the pneumatic trough, and put the delivery tube in position.

Half fill the globe of the funnel with pure concentrated hydrochloric acid [Side-shelf], and admit this to the flask, a little at a time, in such a way that a steady, but not too violent action takes place. When the metal is entirely dissolved, drive all the gas over into the bottle by pouring boiled water once more through the funnel (be careful that no air is carried with the water).

When the gas has acquired the temperature of the water and room, lower the bottle until the level of the water outside and inside is the same. Close the bottle with a cork and remove it from the trough. Weigh the bottle as it stands on the rough scales, and and also completely filled with water, and subtract, to find the volume of the gas. Take the temperature and barometric pressure.

Calculate the weight (1 liter weighs .09 gr. at 0° and 760 mm.) of the hydrogen obtained. Calculate the equivalent weight of zinc, *i. e.*, the weight of the metal which displaces 1 gr. of hydrogen.

b. The experiment may be performed with magnesium (about 0.7 gr. = 65 cm. of No. 23 wire), iron (about 1.5 gr.), or aluminium (about 0.8 gr.) in place of zinc.

In the absence of a dropping funnel, a substitute may be made by connecting a funnel with a straight tube by means of a rubber joint closed with a pinch clamp. Or, the aspirator (Fig. 4) may be used here, the metal (half the above quantities), water, and a smaller tube containing the acid being placed in a test-tube, and the mixing being effected by inclining the bottle after the apparatus is connected.

4. Using the data found in 3, *a*, calculate the weight of hydrogen which would be displaced by the combining weight of zinc obtained in 2. This will be a combining weight of hydrogen with oxygen (16). What substance has this composition?

5. DULONG AND PETIT'S LAW. The specific heats of the metals used in this chapter are:

Aluminium	0.214	Magnesium	0.250
Copper	0.095	Zinc	0.095
Iron	0.114		

Take the values of such combining weights and equivalents as you have found experimentally in 1, 2 and 3 and determine the atomic weights of the metal or metals used.

CHAPTER VII.

WATER AND SOLUTION.

1. PURITY OF WATER. Place a few drops of distilled water on a clean watch glass and evaporate on the sand bath. Do the same with ordinary water. Observe whether any stain remains on the glass. What class of impurities would leave no trace of their presence in this test?

2. UNION WITH OXIDES. Place a pinch of cupric oxide in a test-tube and wash it by shaking with a little distilled water and pouring off the liquid. Add more water and shake again. Test this solution with neutral litmus paper (?). At the same time test a sample of the water with the same paper and compare the tints. Repeat with barium oxide (?).

The behavior of acid-forming oxides has been examined in Chap. IV, 3. Recall the three cases.

3. WATER OF CRYSTALLIZATION.

a. Heat some blue vitriol gently in a porcelain crucible (?). Dissolve the white powder in the minimum amount of boiling water and set the solution aside (?). What chemical action has taken place in each case?

b. [Quant.] Weigh out small quantities (about 1 gr.) of Glauber's salt and blue vitriol in two porcelain dishes; allow them to remain for 24 hours and weigh again [R] (?).

c. Gently warm small quantities of barium chloride, potassium nitrate, magnesium sulphate, alum, and potassium bichromate separately in test-tubes and notice whether they undergo any change [R].

Do all crystalline substances contain water of crystallization? Classify the substances you have examined into two groups with reference to this property.

d. [Quant.] Weigh out about 2 gr. of gypsum in a porcelain crucible. Heat to redness until no further loss in weight occurs, and weigh the calcium sulphate remaining. Assuming the atomic weights of the elements and the formulæ of the sulphate and of water, calculate the formula of gypsum.

4. DELIQUESCENCE. Set some potassium carbonate aside in a small beaker and examine it from day to day.

5. SOLUTION: GASES IN LIQUIDS.

a. Half fill a 1 liter bottle with distilled water, cork and shake vigorously till the water is saturated with air. Take the temperature of the water and the height of the barometer. Measure the content of a flask holding about 100 c.c. and fit it with a cork and delivery tube (Fig. 7). Fill the whole apparatus with the prepared water and boil, collecting the gas in an inverted test-tube. When no more

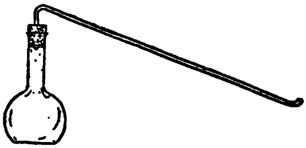

FIG. 7

comes over, equalize the levels and mark the level in the tube with a thin rubber ring. [Cut this from your rubber tubing.] Measure the volume which the air occupied and calculate the volume of air dissolved by 100 c.c. of water at the observed temperature and pressure, correcting for the aqueous vapor present (?).

What proportion of its own volume of air has the water dissolved?

b. [Quant.] Fit up a gas washing bottle and test-tube (Fig. 8), making a slight notch down the side of the cork in the latter to permit the escape of gas. Provide a short piece of wire for hanging the test-tube on the balance. Fill the bottle one-third full of water (use of this?).

Weigh the test-tube and fittings, place in it about 5 c.c. of water, weigh again, and finally support it in a beaker full of cold water. Connect a bottle of liquid sulphur dioxide [Hood] with the washing bottle and turn on a slow stream of the gas. When the water seems to be saturated, stop the gas. Disconnect, dry, and weigh the test-tube once more. Repeat the operation for a minute or so and weigh again. If there is an increase (?) repeat until the weight is constant. Take the temperature (*t*) of the water in the beaker and the height of the barometer (*p*). Calculate the weight of sulphur dioxide dissolved by 100 c.c. of water at the observed *t* and *p*. Calculate the volume which this weight of gas would occupy at *t* and *p*. How many times its own volume of the gas has the water dissolved?

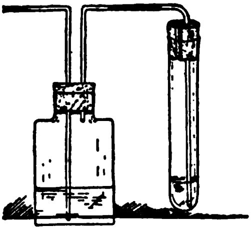

FIG. 8

State the law (Henry's) in accordance with which the amount of the gas dissolved varies with the pressure [R].

6. SOLUTION: LIQUIDS IN LIQUIDS.

a. Take 5 c.c. of alcohol in one test-tube and an equal volume of water in another. Add the alcohol to the water a drop or two at

a time, shake after each addition, and observe whether solution takes place (?). Repeat, adding water to alcohol (?).

b. Repeat *a* with ether and with carbon disulphide in place of alcohol (?), taking care to use dry test-tubes.

7. SOLUTION: SOLIDS IN LIQUIDS.

a. Prepare a saturated solution of potassium bichromate by pulverizing the salt (about 7 gr.), placing it in a flask containing 50 c.c. of water and shaking it at intervals for ten minutes.

Take the temperature of the solution. Weigh [Quant.] into an evaporating dish about 25 gr. of the solution. Evaporate to dryness on the water bath and weigh again. Calculate the weight of bichromate dissolved by 1 liter of distilled water at the temperature observed.

b. Take 6 gr. of the salt and boil with 10 c.c. of water in a test-tube. Has the solubility changed? Allow the clear solution to cool (?). Explain the result.

c. Shake some calcium sulphate with recently boiled distilled water. Does it dissolve? Prove the correctness of your conclusion. Repeat with chalk (calcium carbonate), rejecting the water with which it is first shaken (?).

d. Two immiscible solvents. Place a small particle of iodine in each of three test-tubes and add to one water, to the second potassium iodide solution, to the third ether, and shake each (?). If any iodine remains undissolved, pour off the solution into a clean test-tube. Now add a little ether to the first two, shake again (?), and describe carefully what seems to have happened. Can you deduce from this the relative solubility of iodine in the three solvents?

CHAPTER VIII.

CHLORINE AND HYDROGEN CHLORINE.

1. PREPARATION OF CHLORINE [HOOD].

a. Prepare some strips of filter paper by dipping them in starch emulsion, to which one drop of potassium iodide solution has been added.

Place small quantities of potassium chlorate, minium, and potassium bichromate in as many test tubes and add a little concentrated hydrochloric acid to each. Hang a strip of the prepared paper in each tube (?) and notice also the odor (?). If no action takes place in the cold, apply heat. What property is common to these three substances ?

b. Arrange a generating flask (Fig. 6) and a bottle to wash the gas like that in Fig. 8. Use glass tubes with very short rubber connections here and in 4, *d*, (hydrogen chloride) as rubber tubing is destroyed by these gases. Test the apparatus to see that it is air-tight. Charge the flask by placing in it a handful of coarsely powdered [Iron mortar] manganese dioxide and enough concentrated hydrochloric acid to cover the dioxide. Fill the washing bottle one-third full of water (use of this ?). Notice what happens in the cold before applying heat. Use a shallow vessel filled with boiling water (why not a sand bath or naked flame ?) to warm the flask. Fill four bottles and two test-tubes with the gas by downward displacement, covering them during the process with a card perforated to admit the tube [See note below]. Under what conditions could you collect the gas over water [R] ?

When sufficient chlorine has been collected, filter a part of the residue in the flask into an evaporating dish, evaporate to dryness [Hood] and redissolve in about 40 c.c. of boiling water. If the residue was yellow, from the presence of ferric chloride, add sodium hydroxide solution drop by drop to the hot liquid and stir at intervals. The precipitate will at first be brown (?). Stop as soon as the fresh formations of precipitate are white (?). Heat and stir once more, filter with the assistance of a water pump [See note], and concentrate the filtrate and allow it to crystallize (?) Keep the product for use in 4, *a*.

What data are necessary to enable us to ascertain the formula of manganous chloride and to write the equation representing the above action ?

NOTES.—Be careful not to allow any of the gas to escape into the room. When the gas is not being collected, let it bubble into

caustic soda solution in a test-tube. Empty the flask and bottle finally into the sink in the hood.

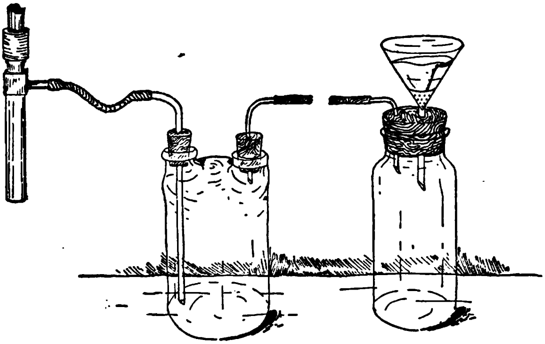

FIG. 9

Much time may be saved, and better results obtained, by using a pump in filtering liquids and in washing precipitates. The apparatus is shown in Fig. 9. Use a small cone made of perforated parchment paper to protect the point of the filter paper. The pump, the safety bottle for protecting the solution from admixture with water from the pump, and the connecting tubes may be obtained from the storeroom [Temp. order].

c. Heat some powdered manganese dioxide in a test-tube with concentrated sulphuric acid. Test the gas which comes off (?) What light does this throw on 1, *b?*

2. PROPERTIES OF CHLORINE [HOOD].

a. In one bottle of the gas scatter a pinch of finely powdered antimony (?) [R].

b. Heat a piece of clean sodium (fingers and knife used in handling it must be dry!) of the size of a pea in a clean, dry deflagrating spoon till it burns, and introduce it into a bottle of chlorine (?) Cover the bottle with a glass plate and examine after the smoke has settled. Dissolve the deposit in 2 c.c. of water, concentrate, crystallize, and examine with a lens (?)

c. Connect a glass tube terminating in a capillary opening with the illuminating gas supply, and lower a small, burning gas jet into the third bottle (?). Blow the breath into the bottle after withdrawing the jet (?).

d. In the fourth bottle place some litmus paper, paper with printing and pen and pencil marks on it, and colored calico, all moistened with water. Observe the effect on each. Explain.

e. To one test-tube of chlorine add a drop of indigo solution and shake (?)

f. Fill a test-tube with hydrogen from a Kipp's apparatus. Bring this mouth to mouth with a test-tube of chlorine and mix the gases by repeated inversion. (Take care not to expose the mixture to direct sunlight.) Hold the mouth of each tube to the bunsen flame (?)

3. NASCENT ACTION. Dilute some potassium permanganate solution with water, and add a few drops of dilute sulphuric acid to it. Divide into two parts. Through one pass a stream of hydrogen gas (?). To the second add some zinc dust (?). Interpret the result.

4. PREPARATION OF HYDROGEN CHLORIDE [HOOD].

a. Place small quantities of ammonium chloride, barium chloride, mercuric chloride, and manganous chloride (obtained in 1, *b*) in as many test-tubes, and add a few drops of concentrated sulphuric acid to each. Describe what happens in each case. Blow moist air across the mouth of the test-tube (?). Lower a glass rod dipped in ammonium hydroxide solution into each [See note below]. Try the effect of heating.

NOTE.—The use of ammonia is not a specific test for hydrogen chloride. It can be used only for ascertaining the presence or absence of any one of several gases which are capable of uniting with ammonia.

b. To a pinch of sodium chloride, add a strong solution of phosphoric acid and heat if necessary (?). Test with ammonia as before.

Why is hydrogen chloride driven out by these acids [R]?

c. To a concentrated solution of sodium hydrogen sulphate add pure [Side-shelf] concentrated hydrochloric acid (?). Examine the result with a lens (?).

d. In a 250 c.c. flask, fitted with dropping funnel, gas washing bottle containing sulphuric acid, and glass delivery tube, place a handful of common salt. Admit concentrated sulphuric acid through the funnel. Collect the gas in three dry bottles by downward displacement. Then attach a nozzle to the tube and prepare a solution of the gas in toluene, if such a solution is not provided on the side-shelf, by allowing the gas to bubble through about 25 c.c. of the liquid in a dry, narrow-mouthed bottle. Preserve this solution from access of moisture by corking it tightly and set it aside for use later (Chap. XI, 1, *g*, and 2, *d*). Next, retaining the nozzle, prepare an aqueous solution for use in 5, by passing the gas through 10 c.c. of water in a test-tube.

Relate this action of sulphuric acid on salt to that in *c*.

5. PROPERTIES OF HYDROGEN CHLORIDE AND HYDROCHLORIC ACID [HOOD].

a. Invert one of the bottles of the gas in the pneumatic trough (?). Relate this property to that observed on blowing moist air into the gas (4, *a*). If any gas remains, what should you expect it to be? Test your conclusion experimentally.

b. Pour a little ammonium hydroxide solution on a slip of filter paper and plunge it into the second bottle (?).

Which of the kinds of chemical change does this illustrate?

c. Devise a way of proving, in a rough way, that the gas is heavier than air, and use the third bottleful for carrying it out.

d. Divide the aqueous solution into three parts. To the first add a piece of zinc (?) To the second add some sodium carbonate solution (?).

Why does hydrochloric acid drive out carbonic acid [R]?

Dilute the third part with an equal volume of water and distribute it between four test-tubes To the first add blue litmus solution or paper (?); to the second a drop of silver nitrate solution (?); to the third a drop of mercurous nitrate solution (?); to the fourth a drop of lead nitrate solution (?). Boil the last three, adding more water if no change occurs at first (?). Afterwards examine the cold liquids (?).

CHAPTER IX.

THE ATMOSPHERE, NITROGEN, AND AMMONIA.

1. CONSTITUENTS OF AIR.

a. Place a large plug of copper turnings in the center of a hard glass tube about 15 cm. long. Fit with corks and short glass tubes, and connect with the short tube of the aspirator. Fill completely with water the bottle and long tube of the aspirator and close the screw clamp. Arrange a vessel to catch the water discharged. Now heat the copper red-hot and then partly open the clamp so as to allow the water to be siphoned off in a slow stream. The air will pass over the heated copper. What change does the copper undergo and what collects in the bottle? After three-fourths of the water has run out, close the clamp, disconnect the hard glass tube, attach a delivery tube in its place, elevate the end of the siphon and insert a small funnel. Pour water into the funnel and drive the gas over into a bottle of water inverted in the pneumatic trough. Ascertain whether this gas supports combustion. Describe the gas as regards color and smell.

Other ways of removing oxygen from the air are described elsewhere (Chap. IV, 5 and lect.).

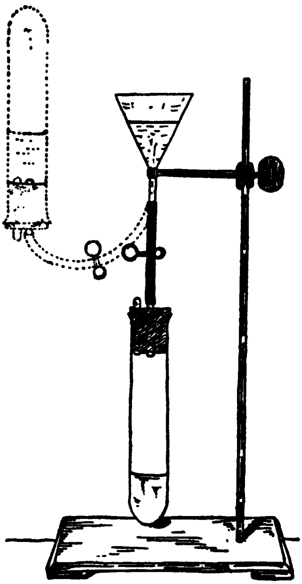

FIG. 10

b. [Quant.] PROPORTION OF OXYGEN TO NITROGEN BY VOLUME. (From Cooley's *Laboratory Studies.* Another method under nitric oxide, Chap. XV 1, *c.*)

The apparatus (Fig. 10) consists of a large test-tube closed with a doubly bored rubber stopper, through which pass a piece of glass

rod and a short glass tube terminating in a nozzle. The latter projects but little beyond the stopper. The glass tube is connected with a funnel by means of a rubber tube 15 cm. long, which can be closed with a spring clamp. The stem of the funnel may be held in a clamp on the ring stand. Disconnect the test tube, remove the piece of glass rod, pour the prepared alkaline solution of pyrogallic acid[1] into the funnel and open the spring clamp slightly so as to allow the solution to fill the entire rubber tube and nozzle. Push the rubber stopper tightly into the test-tube and then insert the glass rod and thus enclose a volume of air equal to the content of the test tube and at the pressure of the atmosphere. During these operations, which should be performed as quickly as possible to avoid exhaustion of the solution by absorption of oxygen from the air of the room, do not warm the test tube by handling. Now open the clamp and allow the liquid to enter. It will flow in until the oxygen is all absorbed. Keeping the clamp open, invert the test-tube and equalize the level of the liquid in both vessels; then close the clamp, restore the test tube to its original position and mark the levels of the liquid and the bottom of the stopper by means of rubber rings.

Disconnect the test-tube, wash out the liquid and ascertain the volume marked off by each ring by weighing water. The smaller is that of the oxygen, the larger that of the air. Calculate the percentage composition of air by volume.

c. Place some clear barium hydroxide solution in the bottom of a beaker and leave it exposed to the air for some hours (?). What substances are found in the air besides those examined here?

d. The weight of 1 l. of air, or of oxygen or nitrogen, may be measured by the method described under carbon monoxide, Chap. XIV, 9

2. NITROGEN. Place about 8 gr. of potassium nitrite and 3 gr. of ammonium chloride in a 250 c.c. flask, add about 15 c.c. of water and clamp the flask by the neck. Warm gently [Caution] and collect the gas in a bottle over water, after time has been given for the

---

[1] Prepared by dissolving 5 gr. of pyrogallic acid in 15 cm. of water and adding a solution of 120 gr. of potassium hydroxide in 88 c.c. of water.

displacement of the air in the flask. Have an evaporating dish filled with cold water in readiness and bring it up over the bottom of the flask when the action becomes too violent.

Ascertain whether this gas supports combustion and describe it as regards color and smell. What impurity causes the slight odor? With what substances will nitrogen unite directly?

3. AMMONIA. Provide a small flask connected with a plain U tube. Place a little water in the bend of the latter so as to close the passage. Put into the flask a mixture of powdered quicklime and ammonium chloride and heat (?). Preserve the solution of ammonium hydroxide. This reaction between strong bases and ammonium salts is used as a test for the latter.

What method would you pursue if you were asked to determine the weight of a liter of ammonia gas? How is the composition of ammonia by volume determined [Lect.]?

4. AMMONIUM HYDROXIDE.

a. Dip a piece of red litmus paper in the solution (?) and expose it to the air for some time (?). Dip a piece of blue litmus paper in dilute hydrochloric acid (?) and expose it to the air for the same length of time (?). Compare the results and interpret. Hold a rod dipped in concentrated hydrochloric acid over the solution (?).

b. Place a little of the solution in an evaporating dish and leave it exposed to the air for twenty-four hours, noticing the odor from time to time (?). In a second evaporating dish warm some of the solution and notice the odor from time to time [HOOD] (?).

c. Neutralize the rest of the solution with dilute sulphuric acid and evaporate to dryness (?) Scrape out the residue and heat it strongly on the inverted lid of a crucible (?).

After completing Chap. XI, enumerate the things which *a*, *b*, and *c* show the solution of ammonia to contain. Explain fully the mechanism of the changes in *b* and *c*.

d. Place some ammonium chloride in the middle of an open, hard glass tube. Support this in a slightly inclined position, put a moist piece of neutral litmus paper in each end, and heat the salt

strongly (?). Watch closely the effect on each test paper (?). What is the action of heat on ammonium chloride? Which gas appeared first at the ends of the tube, and why first at both lower and higher ends? Has gravity any influence on the result?

CHAPTER X.

BROMINE, IODINE, AND FLUORINE, AND THEIR COMPOUNDS WITH HYDROGEN.

1. PREPARATION OF BROMINE AND IODINE.

NOTE.—The elements studied in this chapter and chlorine form a group having very similar properties, and are called the halogens. Recall the facts about chlorine and hydrogen chloride (Chap. VIII) and use them as a guide in trying to understand the chemistry of the rest of the group. The hydrogen compounds, hydrogen chloride, hydrogen bromide, etc., are known as the hydrogen halides.

a. For the action of manganese dioxide on hydrobromic and hydriodic acids (*cf.* Chap. VIII, 1, *b*) see 5 and 6.

b. Mix about 1 gr. of powdered bromide or iodide of potassium with the same weight of coarsely powdered manganese dioxide in a test-tube, and moisten with concentrated sulphuric acid. Warm very gently (?). How does a fluoride behave under these circumstances and why [R]? Answer the same question in regard to chlorides (Chap. VIII, 4, *a*).

What have you ascertained about the solubilities of iodine (Chap. VII, 7, *d*)? The relative solubilities of bromine are similar.

2. PREPARATION OF HYDROGEN HALIDES.

a. Place a little powdered bromide and iodide of potassium in test-tubes and moisten each with concentrated sulphuric acid (?). Warm if necessary. Investigate the result in each case as follows:—

Breathe across the mouth of the test-tube to ascertain the effect of the gas on moist air. What gas previously made showed the same behavior (Chap. VIII, 4, *a.*)? Remembering the similarity between the halogens and their compounds, what do you infer in this case? Confirm this conclusion by lowering a glass rod dipped in ammonium hydroxide solution into the test-tube (?).

What is the color of the gas? What do you infer from this [R]? Did anything of a corresponding nature occur when sulphuric acid acted on a chloride? What is the cause of the presence of the colored substance in this case?

Notice the odor of the gas? Lower into the tube a strip of filter paper dipped in lead nitrate solution [R] (?). By the help of these tests two products may be recognized in the case of bromides, and four in the case of iodides. Write separate equations representing the formation of each. What two properties of sulphuric acid does this experiment illustrate?

b. Cover a square of glass with a thin layer of paraffin by warming it very cautiously far above a bunsen flame and rubbing it on one side with solid paraffin. Moisten about 1 gr. of fluorspar in a leaden dish [Temp. order] with concentrated sulphuric acid. Remove part of the paraffin from the glass by drawing some design with the end of a file. Place the glass on the top of the leaden dish and set the whole above a radiator, at such a distance that the dish will be warmed without risk of the paraffin being melted. After half an hour warm the glass once more and wipe the paraffin off with a piece of filter paper (?). Write equations representing the action, and state what becomes of each of the constituents of the glass [R]. Try the test of a rod dipped in ammonium hydroxide solution and held over the contents of the lead dish (?).

How does a chloride behave under similar circumstances? What difference between the four hydrogen halides do the results in *a* and *b* bring to light?

c. Take small samples of finely powdered bromide and iodide of potassium in separate test-tubes and moisten each with concentrated phosphoric acid solution (?). Warm, if necessary. Observe the odor and apply the ammonia (?) and lead nitrate tests (?) as above. What difference between sulphuric and phosphoric acids do you observe?

d. [HOOD.] Fit up a 250 c.c. flask with a dropping funnel and tube, and connect with a U tube (Fig. 11). Fill the latter with dry broken glass, or porcelain, mixed with a little red phosphorus (why?). Connect the other limb of the U tube with a nozzle dipping under 10 c.c. of water in a test-tube. Place about 5 gr. of red phosphorus mixed with twice its weight of sand in the flask, add 5 c.c. of water, and mix by shaking. Pour into the globe of the funnel about 8 c.c. of bromine. Allow the bromine to flow drop by drop on to the phosphorus, and let the gas dissolve in the water. Record such properties of the gas as you observe. Keep the solution. How is hydrogen iodide made?

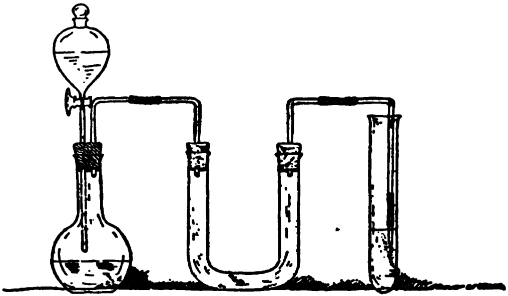

FIG. 11

3. DISPLACEMENT OF HALOGENS BY EACH OTHER [HOOD]. Arrange a small flask with thistle and delivery tubes, omitting the wash bottle, and prepare some chlorine (Chap. VIII, 1 *b*).

a. Pass a few bubbles of chlorine into a little diluted solution of potassium bromide in a test-tube (?). Add a drop or two of the liquid to a test-tube full of starch emulsion (?). Add a little chloroform or ether to the remainder of the liquid and shake (?). Explain. Pass a few bubbles of chlorine through a small portion of the solution of hydrogen bromide obtained in 2, *d* (?).

b. In like manner pass a few bubbles of chlorine through a diluted solution of potassium iodide (?). Add a few drops of the liquid to a test-tube full of starch emulsion (?). Add a little chloroform or ether to the remainder of the liquid and shake (?). Explain. In case the aqueous solution remains brown (why? R), use a little more chlorine and shake again (?).

Have chloroform and ether any chemical action on bromine or iodine? Prove experimentally the correctness of your answer.

c. Examine the action of bromine water on potassium iodide solution in exactly the same way (?).

4. DISPLACEMENT OF SULPHUR AND OXYGEN BY HALOGENS AND BY EACH OTHER.

a. Place 2–3 c.c. of diluted sodium sulphide solution in a test-tube and add bromine water (?).

b. [HOOD.] Place 5 gr. powdered iodine with 50 c.c. of water in small flask. Pass hydrogen sulphide from a Kipp's generator through the mixture till the iodine is all gone and the solution no longer becomes brown on being shaken. Agitate constantly to hasten the process. Describe what happens. Warm and filter the solution. Obtain a distilling flask and condenser [Temp. order] and distill the filtrate fractionally (Fig. 12), collecting first the part that comes over at 100°, then the parts boiling between 100–103°, 103–106°, and so forth. Stop when the liquid is nearly all distilled off. Note the highest temperature reached. Pour the residue into a test-tube and keep the series for use in **6**. Recall the action of chlorine on water in sunlight. What is the action of fluorine on water [R]? In what way do these resemble the action of iodine on hydrogen sulphide? What is the action of oxygen on hydrogen sulphide solution [R]?

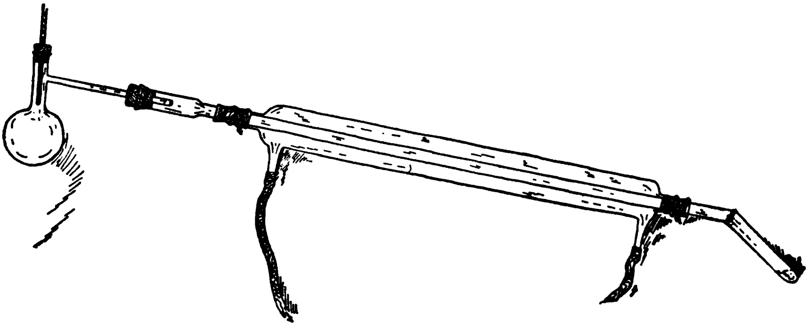

FIG. 12.

5. PROPERTIES OF AQUEOUS HYDROBROMIC ACID. Divide the solution into six portions and examine its behavior towards (a) litmus, (b) zinc, (c) silver nitrate solution, (d) mercurous nitrate solution, (e) lead nitrate solution, (f) powdered manganese dioxide (warm). Boil *c*, *d* and *e*, after adding more water to each (?). Compare these results with those found in the case of hydrochloric acid (Chap. VIII, 5, *d*).

The solution is as good a conductor of electricity as that of hydrogen chloride. What conclusion do we draw from this [R. Chap. XI, 1, *e*] ?

6. PROPERTIES OF AQUEOUS HYDRIODIC ACID. Add silver nitrate to each of the fractions obtained in 4, using only a part of the liquid in the case of the two with the highest boiling points. At what temperature did the strongest solution of hydrogen iodide come over? What peculiarity of aqueous hydriodic acid does the result indicate? What other solutions show the same peculiarity? Compare with the behavior of ammonia (Chap. IX, 4, *b*).

Place a piece of zinc in the remainder of one of the higher fractions (?). Test the other with litmus paper (?), and then add powdered manganese dioxide and warm (?).

On the basis of the experiments in this chapter, devise a system of tests which would enable you to distinguish between chlorides bromides, iodides and fluorides.

CHAPTER XI.

IONIZATION AND INTERACTIONS OF ACIDS, BASES, AND SALTS.

1. IONIZATION. How do we ascertain experimentally whethre a substance is ionized in solution or not, and learn the extent of the ionization [R. Ostwald, "Scientific Foundations," pp. 50–51, pp. 54–56; James Walker, "Introduction to Physical Chemistry"]?

Obtain [Temp. order] a pair of electrolytic cells like that in Fig. 13, and half fill one with dilute sulphuric acid. When the cells are connected in series with the battery, evolution of gas in this cell will indicate that the material in the second cell is a conductor, and that the circuit is therefore complete. In the contrary case, the second substance is a non-conductor, or at most a very bad conductor. If the substance in the second cell is not a metallic conductor (example of this?), what conclusions may be drawn in regard to its condition in each event [R]?

Half fill the second cell with the substances named below in turn. See very particularly that the electrodes in each cell are on opposite sides of the glass partition, connect with the battery and observe the effect in the first cell. When the same experiment has been shown in the lecture-room, the result may be recorded here and the experiment omitted. Wash the cell and electrodes very carefully after each trial.

The substances, or solutions, in *a*, *c*, *d*, *e*, *f*, show the behavior typical of the classes of substances, or their solutions, to which each example belongs. After giving the result in your notes, name the class of bodies which is illustrated in each case.

a. Dry crystallized sodium chloride.

b. Distilled water.

c. Aqueous solution of sodium chloride.

d. Diluted aqueous solution of sodium hydroxide.

e. Aqueous solution of hydrochloric acid.

f. Aqueous solution of sugar.

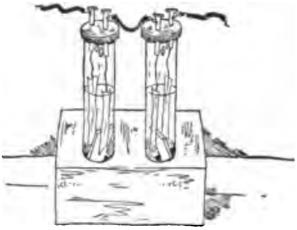

FIG. 13.

g. Dry the cell by washing first with alcohol and then with ether [Instructions]. Test the conductivity of the solution of dry hydrogen chloride in toluene [Prepared in Chap. VIII, 4, *d*, or on side shelf]. What difference between water and toluene do *e* and *g* bring to light? Keep the solution for further use in 2, *d*.

Subsequent chemical experiments with the same, or similar, substances or solutions, will bring out the relation between conductivity and chemical behavior and its explanation.

The chemical nature of the ions into which any compound is split is ascertained by examining the substances set free at the electrodes during electrolysis of a solution and by a study of the interactions of the ions in the solution. The use of the latter method is illustrated in what follows.

h. Give a complete list of the different things (eight of them) which are present in every aqueous solution of common salt. How do the proportions of each of these things vary with changes in the concentration of the solution? Which of the eight are usually most conspicuous in chemical actions? State what happens when these most active constituents are removed from the scene of action [R. Lect.]. What you have stated about common salt holds *cæteris paribus* for all other salts.

2. BASES AND ACIDS. Where experiments in this and the following sections, have already occurred in this outline, simply record the result in this place. In other cases perform the experiments.

a. Examine distilled water in respect to (a) taste, (b) behavior with litmus, (c) conductivity.

b. Dissolve a small piece of sodium hydroxide in water and examine the solution in respect to (a) taste by diluting a little and tasting one drop, (b) behavior with litmus, (c) conductivity. These properties belong to aqueous solutions of all bases.

How can this base be obtained in solid form, starting from sodium and from sodium oxide respectively [R]? Leave a small piece of the solid exposed to the air for 24 hours. Examine the result (?) and add excess of hydrochloric acid (?).

c. Examine an aqueous solution of hydrochloric acid in respect to (a) taste, (b) behavior towards litmus, (c) conductivity [R. Lect.], (d) action on a piece of marble, (e) action on an iron nail. Those properties are shown by all aqueous solutions of acids.

How is the solution of this acid made?

d. Take the solution of hydrogen chloride in toluene and examine it in respect to (a) conductivity, (b) action on a piece of marble, (c) action on an iron nail. Compare and interpret the results in *c* and *d.*

e. Recall the action of concentrated sulphuric acid on zinc (Chap. V, 1, *d*) and the action of dilute sulphuric acid on zinc (Chap. V, 1, *b*), and recollect that the former is a poor conductor and the latter a good conductor. What is the cause of those differences in behavior? To what class of actions does that of concentrated sulphuric acid on a metal belong? How, on the other hand, would you describe the interaction of a metal with an acid in solution?

3. NEUTRALIZATION (cf. 2, first paragraph).

a. Dissolve about 10 gr. of sodium hydroxide in 100 c.c. of distilled water. Place the solution in a burette. Take about 6 c.c. of concentrated hydrochloric acid in an evaporating dish, add 2 drops of phenolphthaleïn solution and allow the alkali to run in drop by drop until the last drop confers the faintest perceptible pink tinge on the solution. Repeat the experiment, if you do not at first succeed in stopping at the right point. Concentrate the solution on the sand bath until a drop deposits crystals on cooling, and then set the dish aside. When sufficient crystals have appeared, dry them with filter paper and examine with respect to (a) form, (b) taste, (c) exposure to moist air, (d) action of a solution on litmus, (e) conductivity of aqueous solution. Construct a table comparing the substance in these respects with the materials from which it was made. Compare the substance with common salt on the side shelf. How would you determine whether a substance obtained in this way contained water of crystallization or not? Make the necessary experiments (?). Wash out both burettes.

The first experiment on the law of definite proportions (Chap. III, 2, *a*) presents another case of neutralization. Write the equations representing these two actions in full and also in the very simplest form [Walker and Dobbin, p. 205; Ostwald, S. F. p. 63].

4. ESTIMATION OF THE RELATIVE ACTIVITY OF ACIDS. The relative "strength" or activity of acids (or bases) can only be measured when the conditions for the acids compared are the same. When the acids are not on the same footing, as in the action of

sulphuric acid on common salt, giving hydrochloric acid, in the absence of much water (Chap. VIII, 4), the fact that the volatile acid is almost entirely driven out does not give any information about the relative "strength" of the two acids. The following experiment illustrates the simplest of the four or five methods of comparing the activity of acids.

a. When methyl acetate is mixed with water, it undergoes hydrolysis very slowly, acetic acid and methyl alcohol being formed: $CH_3.C_2H_3O_2 + H_2O \longrightarrow CH_3OH + HC_2H_3O_2$. Add about 1 c.c. of methyl acetate to 10 c.c. of distilled water in a test-tube, test with neutral litmus paper (?), and cork up and label the mixture. After several days, test once more with litmus (?).

This action of water is found to be greatly hastened by the addition of free acids, although the acids remain themselves unchanged by the process. Equivalent quantities (?) of different acids show very different accelerating powers toward this reaction. The order in which they are placed by measurement of this particular form of activity, however, is the same as that into which they fall when compared by any of the other methods. The extent to which the change has taken place can be measured at any moment by titration with alkali. The quantity of acid which was present at starting being known, the quantity found is the same acid plus the acetic acid set free by the progress of hydrolysis. Subtraction gives the quantity of the latter, and this quantity is a measure of the activity of the accelerating acid. The "strengths" of hydrochloric and sulphuric acids are compared in *b* by this method.

b. Procure two 20 c.c. stoppered graduated flasks and a 10 c.c. and a 1 c.c. pipette [Temp. order]. Mark the flasks so as to be able to distinguish them, and into one measure exactly 10 c.c. of normal (?) hydrochloric acid, and into the other 10 c.c. of normal (?) sulphuric acid. Put exactly 1 c.c. of methyl acetate into each, and fill both flasks with distilled water up to the 20 c.c. mark at once (why at once?). Stopper the flasks tightly, mix the contents, and suspend both so that their necks are just above the water in a large bath heated to about 45°. If the bath is fairly large, further external heating will not be necessary. Allow the flasks to remain in this position for half an hour. While this is going on make some normal (or approximately normal = 4 per cent.) sodium hydroxide and fill a burette with it. Take fresh portions of 10 c.c. of each of the acids and titrate them with the alkali, using two drops of phenolphthaleïn as an indicator. Record the results. These numbers measure the amount of mineral acid at starting in each flask.

When the above time has elapsed, remove both flasks from the bath, transfer the contents of each to a separate beaker, rinsing out the flasks with distilled water. Add two drops of phenolphthaleïn to each portion and titrate with the solution of sodium hydroxide used before. The difference between the volumes of alkali required for the neutralization of 10 c.c. of each acid with and without methyl acetate represents the amount of sodium hydroxide required to neutralize the acetic acid liberated in the hydrolysis. The two values obtained are functions of the activity of the acids. Which acid is more active? What, according to the theory of ionization, is really measured in these experiments?

Does the result of *a* show water to be an acid?

5. ACID SALTS. Fill one burette with potassium hydroxide solution. Add 30 c.c. of concentrated sulphuric acid to 70 c.c. of water and fill the other burette with the diluted acid. Ascertain, as in 3 (*q. v.*), what volume of this alkali will neutralize 5 c.c. of the acid, concentrate by evaporating to about 12 c.c., and allow the resulting solution to crystallize. Dry the crystals on filter paper. To a second portion of the acid, twice as great as before (10 c.c.), add exactly the same amount of alkali, evaporate to about 5 c.c. and treat as before.

Compare the two lots of crystals as regards (a) form, (b) taste, (c) reaction of solution with litmus, (d) water of crystallization. Wash the burettes very carefully to prevent the stopcocks becoming fast.

Name all the things (five of them) which the solution of potassium hydroxide contained. Describe what happens to each of these,

so far as they are changed, in the course of the titration. If the solution had been one of ammonium hydroxide what additional kind of material would have been present and what changes would it have undergone in the course of the neutralization?

[Advanced students.] Why do some acid salts show no acid reaction with litmus? Give an example [R]. Define the terms "normal salt" and "acid salt." Why are some normal salts basic and others acid in their reactions towards litmus? Give examples [R].

What is meant by the term "basic salt?" Give examples [R. Examples for above cases in text-book; theory from lect.].

6. DOUBLE DECOMPOSITION IN SOLUTION (cf. 2, first paragraph).

The mechanism of the following changes, or classes of changes, is to be described in accordance with the theory of ionization.

NOTE:—Aqueous solutions of the substances used in these experiments will be found on the side shelf. Examine the same substance in the solid form when you fetch the solution.

a. Formation of an hydroxide. To some ammonium chloride solution in a test-tube add some sodium hydroxide solution. Observe the odor. State carefully in what this chemical change has consisted and write the equation in full and also in its very simplest form [Walker and Dobbin, p. 205]. Define the term "weak base" and illustrate. This kind of action is often accompanied by precipitation, as in making zinc hydroxide [Lect.].

b. Formation of an acid. Add a few drops of concentrated hydrochloric acid to a concentrated solution of sodium acetate in a test-tube and, if necessary, warm gently. Observe the odor. State carefully in what this chemical change has consisted and write the equation in full and also in its very simplest form [W. and D. p. 206]. Define the term "weak acid" and illustrate. This kind of action is often accompanied by precipitation as in making silicic and boric acids [R].

c. Formation of a salt. Place 3 or 4 c.c. of silver nitrate solution in a test-tube, dilute with water and add potassium chloride solution cautiously until no further precipitation occurs. Filter, concentrate the filtrate and pour it into a watch glass to crystallize. Two salts are formed. Write the general equation and also the two equations representing the formation of the salts separately. Is the formation of a precipitate essential in order that any change may take place [R. Lect.]?

Take 3 or 4 c.c. of silver nitrate solution, dilute with water, and use one fourth for each of the following experiments.

To the first and second portions of the silver nitrate solution add solutions of calcium chloride and cobalt chloride respectively (?). What do these results show the solutions of these chlorides and potassium chloride to possess in common ?

To the third portion of the silver nitrate solution add a few drops of potassium chlorate solution (?). What conclusion may we draw from this result in regard to the ions present in the solution of potassium chlorate ?

To the fourth portion of the silver nitrate solution add potassium cyanide solution [Care ! Poison !] until the precipitate at first formed is redissolved. Now add a drop or two of potassium chloride solution (?). What is the difference between this silver solution and that of silver nitrate as judged by the potassium chloride test ?

Chloroform and chloroacetic acid fail to give a precipitate with silver nitrate. How do these substances differ from chlorides ?

To a few drops of silver sulphate solution in a test-tube add some potassium chloride solution (?). What does this show to be common to the solutions of silver nitrate and sulphate ? What is the difference between the solution of the sulphate and that containing potassium cyanide ?

d. Place in three test-tubes small quantities of solutions of sodium sulphide, sodium sulphate and sodium thiosulphate and add to each a few drops of cadmium sulphate solution (?). Assuming that we know the nature of the precipitate in the one case and the ions in that case, what conclusion do we draw from the behavior of the other two solutions ?

In what way does the lecture experiment with potassium ethyl sulphate and barium chloride illustrate the same points?

e. Put some potassium chromate solution in one test-tube and some chromium chloride solution in another. Add to each a few drops of barium chloride solution (?). Why does the second behave differently from the first?

f. Can reactions like those in *c* (and *d* and *e*) take place without precipitation being observed? What is the cause of the chemical change, if any occurs; and what is the cause of precipitation where it occurs? What is precisely the influence of the latter on the chemical change?

g. Take some of the ordinary calcium chloride solution in one test-tube. Dilute one drop of it with a large amount of water in another. Add a drop or two of dilute sulphuric acid to each (?). Explain.

h. Place small quantities of sodium hydrogen carbonate (bicarbonate) and potassium hydrogen tartrate in a mortar and rub them together (?). Now throw this mixture into a small beaker of water. Contrast effects with and without water and explain.

7. DISPLACEMENT OF ONE ION BY ANOTHER.

a. Place a piece of zinc in a dilute solution of cupric sulphate and set aside till the change is complete (?). Filter and examine the precipitate (?). Treat it with a drop or two of concentrated nitric acid in a test-tube (?), and add ammonium hydroxide to the result (?) Treat a fragment of copper turnings in the same way (?). What does the solution contain? Add colorless ammonium sulphide solution to it (?).

In what way do the experiments in Chap. V, 1, illustrate this kind of action? Answer the same question in regard Chap. V, 2, *a*, and *d*.

The order in which the metals stand in reference to their tendency to enter the ionic condition from the metallic (the order of decreasing solution tension), is as follows:—

Alkali metals.
Alkaline earth metals.
Magnesium.
Aluminium.
Manganese.
Zinc.
Cadmium.
Iron.
Cobalt.
Nickel.
(Tin).
Lead.
Hydrogen.
(Bismuth).
(Antimony).
Copper.
(Arsenic).
Mercury.
Silver.
Palladium.
Platinum.
Gold.

Each will in general displace from a normal solution the ions of any metal below it in the series [R. Electro-Chemistry].

b. Examine your notes on Chap. X, 3 and 4.

What is the action of free chlorine on bromine ions (3, *a*)?

What is the action of free chlorine on iodine ions (3, *b*)?

What is the action of free bromine on iodine ions (3, *c*)?

What is the action of free bromine on sulphur ions (4, *a*)?

What is the action of free iodine on sulphur ions (4, *b*)?

Arrange these four elements in a series similar to that for metals given above. Where would you place fluorine in this series? Can you indicate the approximate position of oxygen (4, *b*)?

8. In previous lecture and laboratory experiments we have observed the formation of acids, bases, and salts in other ways than those illustrated in this chapter. These ways are non-ionic, or not distinctly ionic. Give illustrations of such of these ways as you recall:—acids, one way; bases, one way; salts, three ways. Two other ways of making salts will occur later.

CHAPTER XII.

OXYGEN COMPOUNDS OF THE HALOGENS. OZONE AND HYDROGEN PEROXIDE.

1. HYPOCHLORITES AND CHLORATES [HOOD].

a. Slake a piece of quicklime in a small beaker and add enough water to make a thin paste. Pass chlorine, which has been washed with water (why?), into the mixture for ten or fifteen minutes (?),

cooling the vessel by surrounding it with water during the process (why ?). Immerse a piece of litmus paper (?) and a piece of colored calico (?) and then dip them in dilute sulphuric acid (?).

How could you make a solution of pure calcium or potassium hypochlorite [R] ?

b. Dissolve about 3 gr. of potassium hydroxide in 7 c.c. of water in a test-tube and saturate the hot solution with chlorine. If nothing appears after the solution has cooled, concentrate on the steam-bath. Describe the crystals. Filter, acidify the filtrate with pure nitric acid and test with silver nitrate solution (?). Dry the crystals, heat them in a narrow tube and test for oxygen (?). Use the same chlorine apparatus for 2, *a.*

2. BROMIC AND IODIC ACIDS [HOOD].

a. Take two test-tubes and place in each a few drops of carbon disulphide and 5 c.c. of water. Add one drop of potassium iodide solution to one, and one drop of potassium bromide solution to the other. Pass chlorine, a few bubbles at a time, into them alternately, shaking after each addition of chlorine (?). Continue until no further change occurs. Explain the changes which are observed [R].

b. Take 2 c.c. of potassium bromate solution in a test-tube, add an equal volume of dilute sulphuric acid (?) and divide into two parts. Allow one part to stand to see whether there is any further action (?). To the other part add a single small fragment of iodine and shake for several minutes (?). Pour the solution away from any undissolved iodine and shake the former with a few drops of chloroform (?). Which of these halogens has the greater tendency to unite with oxygen ?

3. OZONE. Place two or three pieces of phosphorus in a bottle, add enough water to half cover them and one drop of potassium bichromate solution. Dip a strip of filter paper in starch emulsion to which a drop of potassium iodide solution has been added. Fasten it by means of a cork in such a way that it hangs down almost to the phosphorus. Allow the apparatus to stand for an hour (?). After the effect appears on the starch paper, try a

paper dipped in manganous chloride solution (?). Return the phosphorus to the supply bottle.

4. PEROXIDES.

a. Suspend some barium peroxide in water in a small flask, add dilute sulphuric acid and shake vigorously for a minute or two in a stream of running water (why?). Filter the mixture and divide into three parts.

To the first, placed in a narrow test-tube, add dilute acidified [cf. Chap. XIII, 3, *c*] potassium permanganate solution (?). Test the gas which comes off for oxygen. By what term should we describe this effect of hydrogen peroxide?

Add the second portion to starch emulsion containing a drop of potassium iodide (?). To the third add some ether (object of this [R] ?) and shake, and then add one drop of potassium bichromate solution and shake again (?).

b. Dissolve a pinch of sodium peroxide (how is this made?) in 10 c.c. of cold water in a test-tube (?). Cool in running water as above. Add two drops of potassium bichromate solution, shake (?), add a few drops of dilute sulphuric acid and shake again (?). Quickly add some ether and shake again (?). Explain all that happens.

c. Suspend lead dioxide and manganese dioxide separately in water and treat with dilute sulphuric acid as in *a*. Apply the bichromate test (?). What are the differences in behavior and constitution between a true peroxide and those oxides which are sometimes called peroxides [R] ?

CHAPTER XIII.

SULPHUR AND ITS COMPOUNDS.

1. SULPHUR.

a. Place a few grams of sulphur in a dry test-tube and heat. Describe all the changes which occur.

b. Pour the boiling sulphur into a beaker of cold water and examine the product. How could you discover whether the change

was due to chemical action on the water or not? In what substance have you found roll sulphur soluble? Find out whether a part of this specimen is soluble in the same substance. Set the rest aside and examine it after a day or two (?).

c. Rub a pinch of sulphur with a globule of mercury in a mortar (?). Recall cases of the union of sulphur with metals which you have met previously.

d. Make a thin paste of flowers of sulphur and distilled water by rubbing them together in a mortar, spread it evenly over the inside of a narrow-mouthed bottle. If it dries quickly, repeat the moistening as often as is necessary. After 24 hours, examine the mass. Notice its odor (?) and hold a rod dipped in ammonium hydroxide solution over it (?). If it has dried up again, mix with a little water. Then filter, using a very small filter paper, and test with neutral litmus paper (?) and with barium chloride solution (?).

e. [HOOD.] Place a few particles of sulphur on the inverted lid of a porcelain crucible and heat strongly (?). Notice the odor of the gas and apply the ammonia test (?). Contrast the results of *d* and *e*,—the effects of oxidizing sulphur in presence and in absence of water.

2. HYDROGEN SULPHIDE [HOOD].

a. Place a little ferrous sulphide in a test-tube. Add some water and then concentrated sulphuric or hydrochloric acid until a moderately rapid evolution of gas ensues (?). Notice the odor of the gas. Use a Kipp's apparatus, and wash bottle for preparing the gas required in 2, *b*, 3, and 4.

b. When the air has been displaced, attach a nozzle and set fire to the gas. What are the products of its combustion? Hold a porcelain dish in the flame (?). Deduce from this observation the chemical changes which probably take place in the flame. What light does this throw on the difficulty in making the substance by direct union of the elements?

c For comparison, treat a little ferrous sulphide in a test-tube. with concentrated sulphuric acid in the cold (?) and then heat (?).

3. Properties of hydrogen sulphide [Hood].

a. Prepare an aqueous solution of the gas and expose the greater part of it to the air for some time in a beaker (?). Preserve the rest for use in 4, *g*.

Place the following substances in test-tubes and pass a vigorous stream of the gas through each for a few moments. Study each action carefully:—

b. Concentrated sulphuric acid (?). What substance might be used for drying the gas, and which substances would be unsuitable?

c. Acidified potassium chromate solution (?). ["Acidified" means that an acid has been added until the solution has an acid reaction towards litmus. Use sulphuric or hydrochloric acid here.]

d. Acidified potassium permanganate solution (?).

e. Ferric chloride solution (?). Filter and add potassium ferricyanide solution to the filtrate (?). For comparison, take ferrous sulphate and ferric chloride solutions in test-tubes, and add the same reagent to each (?).

Recall the action of hydrogen sulphide solution on iodine (Chap. X, 4, *b*). What general property of hydrogen sulphide do these experiments illustrate?

4. Metallic sulphides [Hood].

Pass a stream of hydrogen sulphide into each of the following solutions to saturation (test ?) and note the results:—

a. Cupric sulphate.
b. Antimony trichloride.
c. Lead nitrate.
d. Zinc acetate.
e. Barium chloride.

Add chemically pure hydrochloric or nitric acid [Side shelf] to each of the above and observe the effect. Classify these metals according as their sulphides are soluble in water alone; insoluble in water, but soluble in dilute acids; insoluble in either.

f. Add sodium carbonate solution to lead nitrate solution in a test-tube, filter, and expose the paper with its precipitate to hydrogen sulphide gas (?).

g. Test the rest of the aqueous solution of hydrogen sulphide from 3, *a* with litmus paper (?).

Pass a stream of the gas into a few c.c. of sodium hydroxide solution in a test-tube until the solution is saturated (test ?) (?). Test the solution with litmus paper and divide into three parts.

To the first add dilute hydrochloric acid (?).

To the second add a little powdered roll sulphur and shake from time to time. After half an hour, filter and acidify the filtrate with dilute hydrochloric acid (?). What did the yellow solution contain [R] ? Recall an experiment with iodine which resembles this action of sulphur on sodium sulphide. Filter, wash the precipitate with water, dry it, and test its solubility in carbon disulphide and its combustibility.

Leave the third portion in a partially closed bottle for several days (?). After a change in its appearance is plainly perceptible, add dilute hydrochloric acid in excess (?). Explain.

5. SULPHURIC ACID [Two students working together].

a. Obtain a distilling flask, safety bottle with rubber connections, and Chapman pump from the storeroom [Temp. order]. Fit a 1 liter bottle as in Fig. 14, charge the hard glass test-tube with about 5 gr. of granular pyrite. Place in the distilling flask about 10 c.c. of pure concentrated nitric acid [Side shelf]. The safety bottle, half filled with water to show the rate at which air is being drawn through the apparatus, is attached to the water pump. The total air admitted is regulated by the screw clamp near the pump, while the proportions which pass over the pyrite and carry over the nitric acid vapor respectively are regulated by the other.

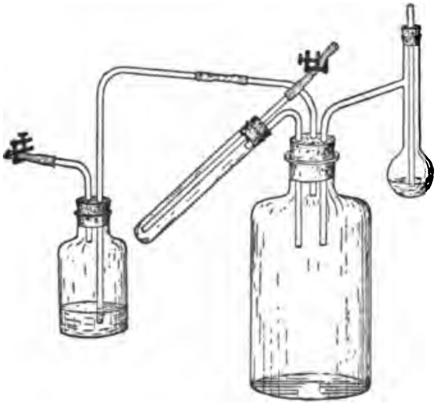

FIG. 14.

First heat the pyrite in a very gentle stream of air until the sulphur burns. Then warm the nitric acid and divert part of the air current so that it may carry over a little of the vapor of the acid. Keep the supply of sulphur dioxide going continuously. Repeat the introduction of nitric acid at intervals, whenever the disappearance of the red fumes in the bottle shows that a further supply is needed.

After a crust of crystals (?) has formed in the bottle (there may be considerable delay before crystallization starts), withdraw the gases from the interior by means of the pump. Detach the bottle, add 4–5 c.c. of water and wash down the crystals with it. Describe all that happens. If more of the product is required, the apparatus may be connected up again and a further supply of sulphur dioxide drawn into the bottle and subsequently more nitric acid vapor can be added. Finally any remaining crystals may be decomposed by water.

Filter the liquid in the bottle through a very small filter paper into a dish, rinsing the bottle with 2–3 c.c. of water, and evaporate on the sand bath [HOOD] until the liquid begins to fume (?). This will remove any nitric or nitrous acid that it may contain. Use the result for *b*.

b. Dilute the product from *a* by adding it to 2–3 volumes of water. Test the solution with litmus paper (?). In one-third of it place a piece of zinc or iron (?). To a small part add barium chloride solution (?). With the remainder make marks on a piece of paper by means of a match dipped in the liquid. Put the match and the paper on a radiator to dry (?).

c. [HOOD]. Take 2–3 c.c. of concentrated sulphuric acid in a test-tube. Suspend a thermometer so that the bulb is completely immersed in the acid. Heat the contents of the tube by means of a small flame and note the temperature at which any effect (?) is observed and that at which it is conspicuous. Be careful not to wash out this tube until the acid has cooled.

6. SULPHATES. Place some cupric sulphate in a hard glass tube and heat strongly with the blast-lamp after all the water has been

driven off (?). Recall action of heat on gypsum (Chap. VII, 3, *d*). Classify sulphates in accordance with this distinction [R].

7. SULPHUR DIOXIDE.

a. Heat a piece of sulphur and a piece of charcoal with concentrated sulphuric acid in separate test-tubes. Notice the odor of the vapor. What property of sulphuric acid prevails in this case? Recall Chap. X, 2, *a* and compare.

Give a list of the properties of sulphuric acid which have been illustrated in 5, *b* and 7.

b. [HOOD], Prepare a flask fitted like that in Fig. 6 and two gas washing bottles like that in Fig. 8. If 8 is omitted, the second bottle will not be required. Twist up some copper turnings [Be careful not to cut the fingers] into bunches, place them in the flask and add 10-15 c.c. of concentrated sulphuric acid. Leave the first of the two wash bottles empty to act as a safety bottle (?) and put an inch or so of concentrated sulphuric acid in the second. See that the apparatus is air-tight.

Heat the flask and contents by means of a sand bath. Leave the cork out at first and suspend in the acid a thermometer. Note the temperatures at which chemical action becomes perceptible (?) and at which it is conspicuous (?). Relate this result to the temperature found in 5, *b*. Connect the apparatus and continue heating to obtain the gas needed in 8 and 9.

Note the appearance of the contents of the flask as the action progresses, and account for it (?). In this connection read 9, *f*.

8. WEIGHT OF A LITER OF SULPHUR DIOXIDE [Quant. HOOD]. Clean and dry a 250 c.c. flask and provide it with a tightly fitting cork. Weigh the flask and cork. This gives the weight of the flask filled with air. Now fill it completely with sulphur dioxide, by downward displacement of air, cork and weigh again. To insure its being full, repeat this operation till no increase in weight occurs. Finally, allow the gas to escape, and determine its volume by filling the flask with water up to the cork and weighing again. Observe the temperature and pressure of the atmosphere.

To obtain the weight of the empty flask and its cork subtract from the weight of the vessel filled with air the weight, under the observed conditions, of a volume of air equal to its content (1 liter of pure dry air weighs 1.293 gr. under normal conditions).

The difference between this corrected weight and that of the flask filled with sulphur dioxide is the weight of the latter. Reduce the volume of the gas to normal conditions and calculate the weight of 1 liter (?) and of 22.39 liters (?).

Enumerate carefully all the sources of error to which you would expect this way of determining the density of a gas to be liable. In doing this, consider each detail of the operation very critically.

9. SULPHUROUS ACID [HOOD].

a. Pass the gas, prepared as in 7, *b*, for a few minutes into a test-tube full of water (?). Test the solution with litmus paper (?).

b. To one-half of the liquid add barium chloride solution (?), and excess of pure hydrochloric acid. Then add bromine water to the same portion (?).

c. Expose the rest of the solution to the air in a beaker for a day or two, testing a few drops with pure hydrochloric acid and barium chloride solution from time to time, as in *b* (?). Relate the result to those in 1, *d* and *e*.

d. Pass a stream of the gas into test-tubes containing solutions of potassium bichromate (?) and potassium permanganate (?), each acidified (cf. Chap. XIII, 3, *c*.) with dilute sulphuric acid, until no further change is observed [R].

e. Collect a bottleful of the gas by downward displacement of air and put in it some moist litmus paper (?).

f. Allow the flask in which the sulphur dioxide was prepared to remain over night, examine and describe the appearance of all its contents carefully. Then, if there is any solid matter in the bottom, pour away the liquid and throw some of the solid into a beaker of water. (If there is no solid, pour part of the liquid into a large amount of water.) What do you observe? Explain.

10. SULPHITES.

a. Heat strongly [Blast-lamp] about a gram of sodium sulphite and sodium bisulphite separately in dry test-tubes until no further change is observed (?). Add dilute hydrochloric acid to each result (?). If free sulphur is observed, account for its formation.

b. Add any dilute mineral acid to either of these salts (?).

11. THIOSULPHATES.

a. How are these salts prepared [R]? Heat strongly a small quantity of sodium thiosulphate in a dry test-tube until no further change is observed. Observe the effect and notice the odor. Add dilute hydrochloric acid to the result (?).

b. Take some sodium thiosulphate solution and add any dilute mineral acid. What appears after a time? Note the odor.

12. REDUCTION OF SULPHUR COMPOUNDS. Mix a pinch of any salt of a sulphur acid with an equal amount of anhydrous sodium carbonate. Slightly char the end of a match and rub it with a heated crystal of sodium carbonate [Instructions]. Moisten the above mixture with water, place some of it on the end of the match, and heat in the reducing region of the Bunsen flame. Put the result on a clean silver coin lying in a watch glass and moisten with water (?). Then add some dilute mineral acid and notice the odor (?). This is a test for sulphur in any form of combination.

CHAPTER XIV.

CARBON.

1. CHARCOAL.

a. Place a small piece of charcoal in a test-tube half full of water (?). Now sink it, if necessary, with copper wire and boil the water for several minutes (?). When the whole has cooled, test once more the tendency of the charcoal to float.

b. Boil dilute solutions of litmus and indigo, separately, with powdered animal charcoal and filter each liquid (?). The activity of the charcoal is much increased by previous heating in a covered crucible.

c. In a hard glass test-tube mix intimately 2 gr. powdered cupric oxide with 1 gr. of powdered wood charcoal and heat [Blast-lamp]. Pass the gases through lime water (?). Examine the residue by rubbing it in the mortar and washing away the lighter particles (?).

2. HYDROCARBONS.

a. Powder some fused sodium acetate and some sodium hydroxide and mix them intimately in approximately equal proportions. Then add a little powdered quicklime and iron filings (these are not necessary for the chemical action in itself), and mix again. Heat the mixture in a hard glass test-tube. Catch some of the gas in a bottle by displacement of water, and explode it with air (?). Burn the gas in a jet and note the degree of luminosity of the flame. Consider how you will ascertain what it forms in burning, and try experiments to settle the matter.

b. Fit a 750 c.c. flask with a doubly-bored cork, through which pass a thermometer and a delivery tube. The former reaches almost to the bottom of the flask. Mix 10 c.c. of alcohol with 40 c.c. of concentrated sulphuric acid by adding the acid gradually to the alcohol and cooling in a stream of water. Place the mixture in the flask. Heat gently on the sand bath and do not allow the temperature to rise above 170° at any time. When the air in the apparatus has been displaced, fill a narrow-mouthed bottle, provided with a rubber or greased glass stopper, with the gas (?) by upward displacement of air.

Add a drop of bromine [HOOD] to the gas and replace the stopper instantly. Observe what happens, and, after a minute, open the bottle under water (?).

Burn a jet of the gas and observe the degree of luminosity of the flame.

Notice whether the gas as generated seems to acquire any odor toward the end of the operation, and explain.

Why is the accepted formula for this gas preferred to the simplest? What volume of oxygen would be required to burn a volume of the gas completely? What would be the volumes of the products?

3. ALCOHOL. Dissolve 20 gr. of molasses in 150 c.c. of water and add a little yeast. Fill the flask to the base of the neck with the mixture, plug the mouth loosely with cotton, and set the whole aside for 3–4 days. At the end of this time warm the solution and test the gas which is given off for carbon dioxide [R. Organic chemistry].

Obtain a condenser and distilling flask, Fig. 12 [Temp. order]. Filter the liquid and distill off about 50 c.c., using an ordinary flask and an L tube to connect it with the condenser. Boil this portion in the distilling flask and catch the part which passes over between 80° and 93°.

Notice the odor of the distillate. Test its reaction with neutral litmus paper. Use one drop to ascertain whether it burns. To the rest add a crystal of iodine and enough sodium hydroxide solution to dissolve it. Shake vigorously and do not add more alkali than is absolutely necessary. Warm the solution and then cool it (?). This is the iodoform test.

4. ACIDS.

a. Add some dilute sulphuric acid to sodium acetate and warm. Notice the odor. Now could you obtain acetic acid? How is it manufactured [R. Organic chemistry]?

b. Take some acetic acid and test its reaction with litmus (?). Recall its action on iron (Chap. V, 1, *c*). Add to it a little litharge (lead monoxide) and boil (?). Filter, if necessary, and crystallize. Describe the product. What is its common name [R.]?

5. ESTERS. Why is the name "ethereal salts," commonly given to these substances, inconsistent with the definition of a salt [R. Organic chemistry]?

a. Dissolve about 1 gr. of sodium acetate in a very little water, add a few drops of concentrated sulphuric acid and two or three drops of alcohol. Warm and notice the odor [R]. This is used as a test for acetic acid.

b. Place in a porcelain dish a piece of fat the size of a pea and add 2 c.c. of alcohol and 5 drops of 50 per cent. sodium hydroxide solution. Stir constantly and boil until the odor of alcohol is no longer perceptible. The alcohol is used as a common solvent for the fat and the alkali. What is the residue [R. Organic chemistry]?

Dissolve the soap in hot water, cool, and to half of the solution add dilute hydrochloric acid and shake vigorously (?). Withdraw the floating coagulum by means of a glass rod, suspend it in water in a test-tube, add a few drops of sodium hydroxide, and heat until solution takes place. What do you conclude from its solubility in alkali?

To the other half of the soap solution add calcium chloride solution (?). Explain the action of hard water on soap solution.

6. CARBON DIOXIDE.

a. Fit up a generating flask with a safety tube and connect with two wash bottles containing water and concentrated sulphuric acid respectively (what is the use of each of these?). Place in the flask some pieces of marble and pour upon them diluted hydrochloric acid. Collect the gas in three bottles by downward displacement.

b. Use the first to ascertain whether the gas is soluble in water or not.

Use the second to compare its weight with that of air. Use baryta water or lime water as a test.

Use the third to test its power of supporting combustion.

c. Lead the gas into a little sodium hydroxide solution in a test-tube until the solution is saturated (test?). Let the solution dry spontaneously (first residue). Heat the dry residue (?) in a test-tube and determine what two things are given off.

To this residue after heating (second residue) add dilute hydrochloric acid till action (?) ceases. Evaporate the solution on the steam-bath and examine and taste this final residue (?).

Having recognized the products of the last action and taking into account the preceding observations, state what the nature of of the second and first residues must have been. Write equations for all actions.

7. MOLECULAR WEIGHT OF CARBON DIOXIDE [Quant.]. Determine the weight of 1 liter of the gas by the method used for sulphur

dioxide (Chap. XIII, 8), and calculate the weight of the gram-molecule-volume at 0° and 760 mm. What further information must we have to enable us to determine the formula?

8. CARBON MONOXIDE.

a. Heat some oxalic acid with concentrated sulphuric acid in a generating flask and fill a bottle with the gas which is given off. Test with lime water (?). With what substance should we wash the gas to remove the carbon dioxide? Arrange a wash bottle to purify the gas. Fill two bottles with the purified gas. Test one with lime water again. If the gas is pure, burn that in the other bottle, add lime water at once, close quickly and shake (?).

b. Devise a way of ascertaining roughly the relative volumes of the two gases generated in *a* and measure the proportion in a test-tube full of the mixed gases.

9. MOLECULAR WEIGHT OF CARBON MONOXIDE [Quant.]. Arrange a 250 c.c. flask as in Fig. 2, using, however a round-bottomed flask for the purpose. Make a mark on the neck at the bottom of the stopper, so as to be able to measure the exact content of the flask up to the stopper. Place 30 c.c. of water in the flask, remove the clip, which must be a strong one, and boil the water with a small flame for about five minutes, so as to drive out all the air. Close the rubber tube with the clip and remove the flame quickly, wipe the flask and allow it to cool. When it has assumed the temperature of the air, weigh the whole carefully, suspending the apparatus on the balance by a wire. Connect with the apparatus delivering pure carbon monoxide, and open the clip a very little so as to admit a slow stream of the gas. When the flask is full, close the clip, disconnect from the generating apparatus, open the clip for an instant to restore the pressure to that of the atmosphere and weigh again. The gain in weight represents the weight of the carbon monoxide. Read the barometer and thermometer. Subtract from the barometer reading the aqueous tension at the observed temperature. Ascertain the volume of the flask by filling with water to the mark and weighing again.

Calculate the weight of 1 liter and of the gram-molecule-volume of the gas at 0° and 760 mm.

To what class of gases would this method of determining the density and molecular weight be applicable?

CHAPTER XV.

OXIDES AND OXYGEN ACIDS OF NITROGEN.

1. PRELIMINARY EXPERIMENTS.

a. Nitric acid [HOOD]. Place a few grams of powdered sodium nitrate in a dry retort or distilling flask, cover it with concentrated sulphuric acid, wait till the substances are thoroughly mixed, and then distill slowly. Use the sand bath as a means of heating and catch the distillate in a flask partly surrounded by water.

Describe the physical properties of nitric acid. Determine its boiling point by boiling it in a distilling flask and arranging a thermometer so that it is immersed in the vapor. Notice the color of the acid. Blow some air through the acid (?). To what was the color due? By what action was the colored substance produced? What property of nitric acid does this indicate?

b. Invert a jar of water in the pneumatic trough and half fill it with oxygen from the iron cylinder. Dilute the nitric acid with half its volume of water in a small flask, fitted as in Fig. 6, add some copper turnings, and, after the air has been displaced, bubble the gas very slowly into the oxygen and agitate continually with water. Notice all the results.

Base a test for nitric acid on this experiment; also tests for oxygen and for nitric oxide.

c. Using these results, devise a way of determining the proportion of oxygen to residual gas in the air and test its accuracy by doing the experiment.

d. Action of heat on nitrates. Heat sodium nitrate in a hard glass test-tube (?). Use the blast lamp, if necessary. Test the escaping gas for oxygen. When gas ceases to be evolved, preserve

the residue for use in 5, *a*. The result is typical of the behavior of nitrates of alkali metals.

Heat 8–10 gr. of powdered lead nitrate in a hard glass test-tube and conduct the gases into sodium hydroxide solution in a test-tube. Continue heating until gas is no longer evolved. What is the residue in the hard glass tube? The result is typical of the behavior of nitrates of heavy metals. Is all the gas absorbed by sodium hydroxide? If not, test the escaping gas for oxygen. Keep the sodium hydroxide solution for use in 5, *b*.

Cautiously heat some ammonium nitrate [Care] and collect the gas in a bottle over water. The result is peculiar to ammonium nitrate. Ignite a little red phosphorus in a deflagrating spoon and plunge it into the gas (?). What other gas is suggested? Suggest a test that would enable you to distinguish between the gases. What change in volume, if any, will accompany this combustion?

Classify nitrates in accordance with their behavior when heated.

2. PRINCIPLES INVOLVED IN MAKING NITRIC ACID.

a. Was nitric acid formed on mixing sodium nitrate and sulphuric acid before distillation began? Solve this question by mixing the materials, adding a very little water [Caution], and trying the test in 1, *b*.

b. Will a nitrate alone behave in the same way toward copper? Try sodium nitrate solution and copper (?)

c. Will other acids behave like sulphuric acid? Try phosphoric acid as in *a*. In view of the result, what should you expect to pass over if the mixture with phosphoric acid were distilled?

d. Is the action in *a* reversible? To answer the question take a few c.c. of concentrated sodium hydrogen sulphate solution and add an equal or greater volume of pure [Side shelf] concentrated nitric acid. Cool the mixture in a stream of water and stir with a glass rod (?). Examine the result with a lens. What is formed? If the action is reversible, write the equation so as to show the existence of an equilibrium. What enabled us to obtain a large yield of nitric in 1, *a* in spite of this?

Give other instances of reversible actions.

3. PROPERTIES OF NITRIC ACID.

a. Is its solution an acid? Prove experimentally.

b. Recall the behavior of concentrated and of dilute sulphuric acid towards metals, and of the former towards non-metals.

Try the action of (1) magnesium, (2) zinc, (3) copper separately on concentrated and on dilute nitric acid respectively. Explore the whole action thoroughly in each case as follows:—

Place the metal in a small flask fitted with a delivery tube, add the acid, and collect the gas over water after the air has been displaced from the apparatus. Observe whether nitrogen tetroxide is is formed. Devise a way of separating nitric oxide from hydrogen, in case the gas should contain any of the latter. Examine it for each of these substances. If ammonia is formed by complete reduction of the nitric acid, where will it be found, and in what condition? Test for its presence. Isolate the form of combination which the metal has assumed, by evaporating the solution to dryness on the steam bath [Hood], and determine its nature. In view of the action of nitrogen tetroxide on water (1, *b*), explain the effect of diluting the acid that is used with the metal. Conversely, the result with concentrated acid is explained by 4, *a*.

c. Try the action of tin on concentrated nitric acid (?). When the action has exhausted itself, add water and boil. Filter through a small filter paper, and wash the precipitate with water until the filtrate is neutral. Devise a way of showing whether the remaining solid is a nitrate or not, and try it (?).

d. Try the action of sulphur on concentrated boiling nitric acid (pure). Is there any evidence of action? If so, find out what form of combination the sulphur has assumed.

What property of nitric acid seems to be most prominent? What points of resemblance and of difference does nitric acid show when compared with sulphuric acid?

e. Dip a piece of wool in concentrated nitric acid [R] (?).

Give the three chemical properties which you have found to characterize nitric acid.

f. Aqua regia. Add concentrated hydrochloric acid to nitric acid, warm, and notice the appearance and odor (?). When gold and platinum (the same is true of other metals *a fortiori*) are placed in *aqua regia* they are dissolved and chlorides are formed. These metals are insoluble in dilute acids (see table of solution tensions, Chap. XI, 7). Explain their solubility in this mixture. What other reagents would dissolve them on the same principle (Chap. VIII, 1, *a*)? Which of the three properties of nitric acid is here brought into play?

4. NITRIC OXIDE.

a. Prepare the gas by the action of copper on diluted nitric acid. Pass the gas through warm concentrated nitric acid (?).

b. Prepare a solution of ferrous ammonium sulphate and divide into four parts. Pass the gas, which must be colorless, through one part (?)

c. Acidify the second portion of the ferrous ammonium sulphate solution with sulphuric acid, heat to boiling, and add two drops of nitric acid (?). To ascertain what the solution contains, add ammonium hydroxide (?) For comparison, add ammonium hydroxide to the third portion of the ferrous solution (?) and to ferric chloride solution (?)

d. Delicate test for nitric acid, or a nitrate. Add a very little sodium nitrate solution to 2–3 c.c. of the ferrous solution in a test tube and pour concentrated sulphuric steadily down the side of the tube so that it may form a layer at the bottom. Notice the brown ring and explain.

5. NITROUS ACID.

a. Dissolve in water the residue from heating sodium nitrate in 1, *d.* If it is necessary to repeat, melt the nitrate with a piece of lead in a crucible and stir with a file (?) This gives the same product more easily (why?). To the aqueous extract, add dilute sulphuric acid. Contrast the action with that on a nitrate (?).

b. Examine the solution, obtained by passing the gases from lead nitrate into sodium hydroxide in 1, *d*, for nitrite, by acidifying with dilute sulphuric acid (?). Add a drop of this mixture to some starch emulsion containing a drop or two of potassium iodide solution (?). To a small portion of the same mixture add a drop of diluted potassium permanganate solution (?). What substance is shown to be present by these three reactions? Try these three tests with sodium nitrite solution (?).

Boil the remainder of the acidified mixture until red fumes cease to be evolved. Then insert a piece of copper (?). What substance is shown to be present by this reaction? Combining these results, what do you infer was the action of nitrogen tetroxide on sodium hydroxide?

CHAPTER XVI.

PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH.

1. **PHOSPHORUS.** What differences in behavior do the two allotropic modifications of phosphorus exhibit [R.]? What is formed when phosphorus unites directly with oxygen? Answer from previous knowledge.

2. **PHOSPHINE** [HOOD]. Place a small piece of calcium phosphide in water or dilute hydrochloric acid in a beaker (?). Relate this to ways of making other hydrides of non-metals (*e. g.*, ammonia, hydrogen sulphide, and acetylene) from compounds of the non-metal with a metal.

3. **HALIDES OF PHOSPHORUS** [HOOD]. The action of water on the tribromide (Chap. X, 2, *d*) and on the triodide (Lect.) have already been noticed.

a. Place 1 c.c. of phosphorus trichloride [Store-room] in a test-tube (?). Blow the breath over the mouth of the tube (?). Add water a drop at a time (?). Add more water and boil. Pass hydrogen sulphide through the solution (?).

b. Place a pinch of phosphorus pentachloride on a watch glass. Blow the breath over it (?). Throw it into some water in a test-tube (?)and boil. To part of the solution add excess of silver nitrate

solution (?). Filter. What remains on the filter? To the filtrate add ammonium hydroxide drop by drop (?). The nature of this precipitate is learned in 4, *a*.

4. PHOSPHORIC ACID.

a. Heat a little red phosphorus with diluted nitric acid (?). When the action has ceased, filter, if necessary, and evaporate the filtrate to dryness on the steam bath (?). Redissolve the sirup which remains in water. Test the solution with litmus paper (?). Add silver nitrate solution. The precipitate is silver orthophosphate (a black precipitate, due to the presence of phosphorous acid, may sometimes be formed). What was the acid?

b. Throw a pinch of phosphorus pentoxide in minute portions at a time into cold distilled water in a test-tube (?). Allow the solution to stand for a few minutes, or until it becomes clear. Add silver nitrate solution (?).

5. PHOSPHATES.

a. Test some sodium phosphate (secondary sodium orthophosphate) solution with neutral litmus paper (?). Add silver nitrate solution (?). Test the filtrate from this with litmus again (?). Are acid salts always acid towards litmus? If not, explain why they are not.

Add a little ammonium hydroxide and ammonium chloride solution to magnesium sulphate solution. Add some of this "magnesia mixture" to sodium phosphate solution (?). Describe the precipitate.

b. Heat a little dry sodium phosphate in a crucible strongly for twenty minutes, or save time by using the blast-lamp (?). When the residue is cold, dissolve it in water and add silver nitrate solution (?). Contrast with the precipitate from unignited phosphate (5, *a*) and compare with that in 4, *b*.

c. Heat a little microcosmic salt strongly in a test-tube and notice its behavior and odor (?). Dissolve the residue in water and add silver nitrate solution (?).

Make a bead of microcosmic salt on a platinum wire and fuse with it a single minute particle of cupric oxide (?).

6. ARSENIC.

a. Heat a particle of arsenic on a crucible lid (?). Notice its behavior and the odor. Do the same with a particle of realgar (?).

b. Boil a little powdered arsenic with nitric acid. Is there any evidence of action? Preserve the solution for examination under 9. [Do 8 next and then return to 7.]

7. ARSINE [HOOD. CARE. POISON]. Arrange a wide test-tube with safety and delivery tubes and nozzle to generate and burn hydrogen. Place in it a piece of chemically pure zinc and add pure hydrochloric acid [Side-shelf]. When the air has been displaced [Care], light the gas and hold a crucible lid in the flame (?). If there is no deposit, add a drop or so of the solution of arsenic trichloride (8, *b*), observe the appearance of the flame and obtain deposits on the crucible lid and in two evaporating dishes (?). What kind of chemical change takes place in the flame? Heat the tube through which the gas passes to the nozzle with a bunsen flame (? Marsh's test). When these experiments are completed, fill the test-tube with water to stop the action.

Apply cold dilute nitric acid to the first spot by means of a glass rod (?).

Apply bleaching powder solution to the second in the same way (?).

Treat the third with yellow ammonium sulphide solution (?).

8. ARSENIC TRIOXIDE.

a. Boil a pinch of the trioxide with sodium hydroxide solution (?). To what class of oxides does this one appear to belong?

b. Boil a pinch of the trioxide with concentrated hydrochloric acid (?). Dilute with a little water and keep part of the solution for 7. To what class of oxides does it appear now to belong?.

Pass hydrogen sulphide from a Kipp's apparatus through the rest of the solution (?). Recall result of 3 *a*. Now neutralize the liquid with ammonium hydroxide (why? If you do not know, add some ammonium sulphide to dilute hydrochloric acid), and add either colorless or yellow ammonium sulphide solution (?). Acidify the solution strongly with hydrochloric acid (?).

c. Seal one end of a small piece of glass tubing. Mix a pinch of the trioxide with a little powdered wood charcoal. Place some of the mixture in the bottom of the tube, with a little fresh wood charcoal above, and heat strongly (?).

9. ARSENIC ACID. Neutralize the solution of arsenic in nitric acid (6, *b*) with ammonium hydroxide, avoiding excess. Divide into two parts. To the first add silver nitrate solution (?). To the second add "magnesia mixture" (?). Recall 5, *a*, and compare.

10. ANTIMONY. Behavior similar to that of arsenic.

11. STIBINE. Follow all directions in 7, using antimony trichloride solution in place of that of arsenic trichloride.

12. ANTIMONY TRICHLORIDE.

a. Place some of the crystals in a test-tube and add a little water (?). Test the liquid with litmus paper (?). Add more water, warm, and make a clear solution by adding small quantities of concentrated hydrochloric acid (?).

b. To half of this solution add a large amount of water (?). What kind of action is this? Add concentrated hydrochloric acid again (?). How does this illustrate mass action? Write the equation which combines both actions.

How could you show that the trichloride is only partially hydrolyzed by water, leaving a basic salt (with phosphorus trichloride the hydrolysis was complete.)?

c. Through the rest of the trichloride solution pass hydrogen sulphide from a Kipp's apparatus (?). Filter, and pour hot yellow ammonium sulphide solution on the precipitate (?). Acidify the solution in ammonium sulphide with excess of hydrochloric acid (?).

13. ANTIMONY TRIOXIDE. Heat some powdered antimony with concentrated nitric acid (?). How does this differ from the behavior of arsenic (6, *b*) [R]? How could you ascertain whether the result was a nitrate or not? Filter.

Boil one half of the powder with hydrochloric acid (?). What kind of oxide does this show it to be?

Boil the other half with sodium hydroxide solution (?). What kind of oxide does this show it to be?

14. BISMUTH. Prepare a match as in Chap. XIII, 12 (match test). Place on the end a moistened mixture of bismuth nitrate and anhydrous sodium carbonate and heat in the reducing region of a small bunsen flame. Break up the charred match gently in water in the mortar, wash away the lighter particles and examine the residue (?).

15. SALTS OF BISMUTH.

a. Add water to some crystals of bismuth nitrate in a test-tube (?). Obtain a clear solution by adding small quantities of concentrated hydrochloric acid.

b. To one half of the solution add a large amount of water. Write the equation to show that an equilibrium exists.

c. Pass hydrogen sulphide through the remainder of the solution from *a* (?). Filter and treat the precipitate with warm yellow ammonium sulphide. Filter and acidify this solution. What is the precipitate? Was the bismuth sulphide dissolved? Compare the result with that in 8, *b* and 12, *c*. How could you separate the sulphides of arsenic and antimony from that of bismuth?

CHAPTER XVII.

SILICON AND BORON.

1. SILICA. Mix 1 gr. of finely powdered silica with 4–5 gr. of anhydrous sodium carbonate. Make a small watch-spring spiral on the end of the platinum wire [Instructions] and, by alternately heating in the bunsen flame or blast-lamp, and dipping in the mixture, obtain a large bead and heat it strongly till all action (?) seems to have ceased. Place the bead in a test-tube and repeat the process. Dissolve the beads in a small amount of water. Add hydrochloric acid a drop at a time until the solution is strongly acid (?). Evaporate the solution to dryness on the sand bath (?). Treat the residue with warm water, wash the whole contents of the dish into a test-tube and examine (?).

2. A SILICATE. Mix dry potassium carbonate with anhydrous sodium carbonate in equal proportions in a mortar. Coil the platinum wire to watch-spring form. Mix a little powdered talc (is this soluble in water? What is its common name?) with 6–7 times as much of "fusion mixture" and hold some of the result on the platinum wire in the flame of the blast-lamp till it is completely melted and all action (?) has ceased. Repeat till several beads are obtained. Treat the beads with boiling water in a test-tube until they are completely disintegrated. Filter through a small filter paper and wash the precipitate with water. Preserve this filter paper and precipitate for use later. Acidify the filtrate with concentrated hydrochloric acid and proceed as in 1.

Make a hole in the paper and wash the precipitate obtained above into a test-tube. Add dilute hydrochloric acid and warm (?). Filter, if necessary, and add ammonium hydroxide to alkaline reaction (?). The precipitate is aluminium hydroxide. Boil and filter. To the filtrate add a few drops of ammonium hydroxide, some ammonium chloride solution and some sodium phosphate solution and shake (?). Compare with Chap. XVI, 5, *a*.

3. BORIC ACID.

a. Dissolve some borax in distilled water. Test this solution and a sample of the distilled water simultaneously with neutral litmus paper, and, by comparing tints, determine whether the solution has any reaction (?).

Put two drops of the solution into a test-tube and dilute with water till the tube is two-thirds full. To the remainder add silver nitrate solution (?). Add silver nitrate solution to the very dilute solution also (?). The difference is more marked if the dilute solution is first warmed. For comparison add silver nitrate solution to diluted sodium hydroxide solution (?). What conclusion do you draw in regard to the action of water on borax? Write the equation. Is the action reversible?

b. Make a strong solution of borax in boiling water in a test-tube. Add concentrated hydrochloric acid until the solution is strongly acid and set aside to cool (?) Filter, press out the mother liquor, and wash the crystals with a few drops of cold water. Dissolve in the minimum amount of boiling water and set aside again. Filter, and wash the crystals as before.

Dissolve part of the crystals in hot water and test the reaction of the solution with neutral litmus paper, using the same precaution as in *a* (?). What conclusion do you draw in regard to boric acid? Dip a strip of turmeric paper in the same solution, wrap it round the upper part of the test-tube and boil the solution until the paper is dry (?). Touch it with a glass rod dipped in sodium hydroxide solution (?). This is a test for boric acid.

Treat the rest of the crystals with cold sodium hydroxide solution (?). Explain the formation of boric acid and its solubility in bases according to the ionic theory.

c. Place on separate parts of a watch glass a drop of concentrated sulphuric acid, a drop of glycerine, and very little powdered borax. Rub the end of a platinum wire in each of these. Bring the end of the wire slowly up to the outer edge near the bottom of a small Bunsen flame. Is the flame colored? This is a test for a borate.

CHAPTER XVIII.

METALS OF THE ALKALIES.

1. POTASSIUM HYDROXIDE.

a. Dissolve about 30 gr. of potassium carbonate (what is the source of this salt?) in 200–300 c.c. of water in a large evaporating dish and heat to boiling. Slake 15–20 gr. of quicklime in a beaker (?), using heat if necessary to start the action, and make the product into a very thin paste with water. Add this gradually, and with constant stirring, to the boiling solution (?). Continue boiling for a few minutes. (Why are iron utensils exclusively employed in this operation when it is performed on a large scale?) Let the solution settle in a beaker and, when it is cold, decant the clear liquid (why not filter it? Try to filter the turbid liquid which

remains and notice the effect on the filter paper). Use the solution in *b* and *c*.

b. Alkalimetry. Find the strength of this solution by titration. To do this, measure 10 c.c. of the clear solution into a small flask. Dilute with about four times its volume of water. Fill a burette with normal hydrochloric acid. Add some phenolphthaleïn solution to the alkali and run in the acid cautiously until the red color just disappears. Notice the volume of acid used. One liter of the acid contains 36.5 gr. of hydrogen chloride. Calculate the weight of potassium hydroxide per liter in the alkaline solution (?). Express this also in terms of a normal solution containing 56 gr. per liter (for example, 28 gr. per liter would be .5 normal).

What kind of hydroxides alone can be made by this method? Which hydroxides are of this kind [R]?

c. Reaction of OH ions. Place small quantities of the following solutions in separate test-tubes and add some of the solution of potassium hydroxide to each: ferric chloride (?); cupric sulphate (?); mercuric chloride (?) [R]. Boil the contents of each test-tube.

What kind of hydroxides can be made by this method? Do any metals fail entirely to form hydroxides [R]?

2. **PREPARATION OF POTASSIUM NITRATE.** Dissolve 25 gr. of sodium nitrate and 22 gr. of potassium chloride in 50 c.c. of water and evaporate to half the volume on the sand-bath. Decant the hot, clear liquid from the crystals and set it aside. Throw the crystals which appeared during boiling at once onto a filter and rapidly press out the rest of the mother liquor. Examine the form of the crystals and ascertain what they are. (If they are too small, recrystallize a part slowly from water in a beaker in order to learn their form.) When the decanted liquid is cold, press the product on a filter likewise. Examine this set of crystals as before. [R. cf. figures in Roscoe and Schorlemmer.] Compare both with the original substances.

Explain the chemical change. The following table gives the solubilities of the four possible salts:

	Grams in 10 c.c. of water	
	10°	100°
Potassium nitrate	2.1	24.6
Sodium chloride	3.6	4.0
Potassium chloride	3.1	5.6
Sodium nitrate	8.1	18.0

Explain why purer potassium nitrate can be obtained by recrystallizing the product from water. Whence the necessity for making the salt commercially by this method at all?

3. POTASSIUM CYANIDE [POISON]. How is this salt obtained? Place 2 c.c. of potassium cyanide solution in an evaporating dish and add yellow ammonium sulphide solution until the color no longer disappears. Evaporate to complete dryness [HOOD], take up a part with water, and add ferric chloride solution (?). A black precipitate (?) indicates that the heating was not sufficient. If this appears, heat the remainder once more and try the action of ferric chloride again. What property of the cyanides does the first part of this experiment illustrate [R]?

4. REACTIONS OF POTASSIUM SALTS.

a. Heat a little solid potassium nitrate on a clean platinum wire. Notice the color of the flame and examine with the spectroscope. Make a diagram showing the positions of the lines with reference to the D line, which, on account of the sodium present, is shown by all flames in the laboratory.

b. To a strong solution of the nitrate (made by warming), add tartaric acid solution. Shake the mixture and cool in a stream of water (?). Describe the product. Filter, and wash the precipitate with a little alcohol. Dry by pressing between filter papers. The nature of the product (?) may be inferred from the results of *c* and *d.*

c. Dissolve a little of the precipitate in warm water and test its reaction with litmus paper.

d. Place half the remainder in a test-tube and add sodium carbonate solution a drop at a time, noticing all that happens (?). Then add concentrated hydrochloric acid, a drop at a time, to the

resulting solution (?). Stir vigorously with a glass rod at intervals. Finally try the effect of an excess of hydrochloric acid (?).

e. Heat the rest of the precipitate strongly in a porcelain crucible (?). Extract with hot water, filter, and add any acid to the filtrate (?). The ignition of all potassium or sodium salts of organic acids gives the same result.

f. To potassium chloride solution, add picric acid solution (?).

What is shown to be present in a solution when we get the tests in *b* and *f?*

5. SODIUM. Recall the properties of the metal as you have met them in previous exercises. From previous knowledge compare its behavior with that of zinc and copper towards (*a*) air; (*b*) water; (*c*) acids. What mineral is the source of the metal and all its salts?

6. SODIUM CARBONATE BY SOLVAY PROCESS. Take 100 c.c. of ammonium hydroxide solution, dissolve in it 10 gr. of powdered ammonium carbonate by shaking, and then saturate the solution completely with sodium chloride by agitation with powdered salt in a corked bottle. Decant the clear liquid into another bottle, fitted with cork and two tubes, one of which reaches to the bottom. Through the latter pass in carbon dioxide from a Kipp's apparatus until the solution is saturated. During the absorption of the carbon dioxide, the exit tube should be closed to prevent waste of the gas. Close the tubes with caps of rubber tubing closed with glass rods [Instructions] and set aside over night (?). Filter off the deposit and dry by pressing between filter papers.

Dissolve a little of the solid in water and test the reaction of the solution with litmus (?).

To part of the solid add any dilute mineral acid (?).

Heat the rest in a test-tube and ascertain what gases are evolved. When gas ceases to be given off, dissolve the cold residue in a very little water, test the reaction of the solution with litmus paper (?), and let it crystallize (?). Ascertain the effect of exposure to air (?) and the action of acids (?) on the crystals.

The solubilities at 20° of the bicarbonate and carbonate in 100 parts of water are 9.6 and 92.8 respectively. Explain why the bicarbonate is made first and then the carbonate from it.

7. REACTIONS OF SOLUBLE CARBONATES: CO_3 IONS. Add sodium carbonate solution to solutions of barium chloride (?), lead nitrate (?), chromic chloride (?), cupric sulphate (?). Add the carbonate cautiously at first, note the gas given off in some cases and account for its formation. Filter the contents of each test-tube and wash each precipitate with water. What are those precipitates? Test your conclusion by a suitable experiment in *each* case.

Save part of the lead compound and, when it is dry, heat it in a dry test-tube and ascertain what gas is given off (?). What carbonates show this behavior [R]?

8. PURIFICATION OF SODIUM CHLORIDE. Wash some crude salt with water and then prepare about 150 c.c. of a cold saturated solution by grinding the salt in a mortar with the water. Place it in a beaker and pass hydrogen chloride into the solution. Prepare this gas by placing a handful of common salt in a generating flask, covering it with concentrated hydrochloric acid and allowing concentrated sulphuric acid to fall into it from a dropping funnel. Deliver the gas into the solution through a thistle tube with the mouth downwards (why use this tube?). When considerable precipitation has occurred, filter by putting a clean silver quarter in a funnel, pouring the liquid and crystals upon it and pressing with a spatula.

Explain why the salt is precipitated. If sodium sulphate or magnesium chloride or some other salt had been mixed with the salt, would they have been thrown down [R]? In other words, why does this process give a means of purification? This question may be answered after the experiments in 9.

9. IONIC EQUILIBRIUM.

a. Take three portions of distilled water and add to each a little methyl orange solution. To the first two add a little acetic acid (?), to the third a drop or two of hydrochloric acid (?). What kind of ions is absent when the indicator is yellow? Add some

solid sodium chloride to the first and stir (?). To the second add solid sodium acetate and stir (?). Explain the difference in behavior. To the third add solid sodium chloride and stir (?). Explain absence of effect.

b. Take three portions of a saturated solution of potassium chlorate in as many test-tubes. (This and the following solutions must be shaken to insure saturation if there is a deposit in the bottles.) Add to the first saturated sodium chloride solution (?), to the second saturated potassium chloride solution (?), to the third saturated sodium chlorate solution (?). Allow them to stand for a minute or two before drawing any conclusion. Explain. The experiments will fail if the solutions are not saturated.

10. REACTIONS OF SODIUM SALTS. Try the flame test and examine with the spectroscope (?). Add tartaric acid (?) and picric acid (?) solutions to separate portions of diluted sodium chloride solution. Compare with results under potassium.

11. AMMONIUM SALTS. What is the effect of heating ammonium salts (Chap. IX, 4, *d*)? Heat some ammonium phosphate in a hard glass test-tube (?). Dissolve the residue in water and test with litmus paper.

Try the flame test with an ammonium salt.

To two portions of diluted ammonium chloride solution add tartaric acid solution (?) and picric acid solution (?) respectively. To a third portion add a strong base and warm (?). Notice the odor. How could you distinguish between solutions containing ammonium and potassium salts?

Make a list of the salts of potassium, sodium, and ammonium which are least soluble [R and exps.].

CHAPTER XIX.

METALS OF THE ALKALINE EARTHS.

1. Heat 2–3 gr. of powdered marble for fifteen minutes in an open porcelain crucible, with a blast-lamp (?). Add a little water to the product when it has cooled (?). (Has water any effect on

marble?) Test the reaction of the liquid with litmus. What was formed by heating marble? The action is reversible. (How is this suggested by the behavior of mortar?) On what will the re-formation of marble depend at any given temperature (W. and D., p. 155)?

2. LIME WATER. Slake a small piece of calcium oxide and shake the product with half a liter of distilled water, let the solution settle, and use the clear liquid.

a. Blow air from the lungs by means of a tube through a part of the lime water (?). How could you determine the proportion of carbon dioxide in a sample of air?

b. Pass carbon dioxide from a Kipp's apparatus persistently through the remainder of the lime water (?). Boil a part of the resulting clear solution (?).

3. REACTIONS OF CALCIUM SALTS. Use calcium chloride solution and dilute it for *b*, *c*, and *d*. [In this and all following paragraphs headed "reactions," where diluted solutions are spoken of, the strong solutions on the side shelf must be diluted with three to four times their volume of water to secure good results.]

a. Try the flame test and examine with the spectroscope (see that the platinum wire is clean). Make a sketch of the spectrum showing the positions of the lines with reference to the sodium and potassium lines.

b. To a solution containing calcium ions add ammonium carbonate solution (?).

c. To another portion of the solution add oxalic acid solution (?) and then ammonium hydroxide (?). If you do not see the use of the latter, add hydrochloric acid to the result (?) and explain. The action is reversible.

d. To another portion add excess of dilute sulphuric acid (?). Filter, and neutralize the filtrate roughly with ammonium hydroxide. To this solution add ammonium oxalate solution (?), and explain (Chap. XI, 6, *g*). Is the sulphate or oxalate of calcium more soluble?

4. **Reaction of strontium salts.** Use strontium chloride solution and dilute it for *b*, *c*, and *d.*

a, *b*, *c.* Same as in 3.

d. To a portion of the solution add dilute sulphuric acid in excess (?). Filter, roughly neutralize the filtrate with ammonium hydroxide, and add ammonium oxalate solution (?). Compare the amount of this precipitate with that in the corresponding place in 3, *d* (?). Is the sulphate or oxalate of strontium more soluble ?

To a fresh portion of the strontium chloride solution add a solution of calcium sulphate (?) made by shaking a little of the salt with water and decanting, and explain.

5. **Reactions of barium salts.** Use barium chloride solution and dilute it for *b*, *c*, and *d.*

a, *b*, *c.* Same as in 3 and 4.

d. To a portion of the solution add dilute sulphuric acid (?). Filter, neutralize with ammonium hydroxide, and test with ammonium oxalate.

To another part of the solution of barium chloride add a solution of strontium sulphate (?) made by shaking the salt with water and decanting, and explain.

Arrange the sulphates of these three metals in order of solubility. How could you tell a solution containing the ions of a member of this family from one containing those of the previous family ? Give two methods of distinguishing between the members of the present group.

6. **Insoluble sulphates.** To a little lead nitrate solution add dilute sulphuric acid (?). Which sulphates have you found to be insoluble ? These complete the list, as far as common metals are concerned.

7. Take three dry test-tubes, apply to the instructor for three "unknown" substances, and ascertain what each is, by the use of any experiments you can devise.

Suggestions: Note physical characters, odor, solubility in water and reaction of the solution towards litmus, effect of heating in a dry tube, effect of heating with concentrated sulphuric acid. Before trying the last two tests, make a list of all the gases which may be expected, the means of identifying each, and the corresponding inferences with regard to the unknown substance. Test gases given off according to circumstances. The results of these experiments will suggest further work. The metals may be identified by the reactions given in Chaps. XVIII and XIX.

CHAPTER XX.

COPPER AND SILVER.

1. CUPROUS CHLORIDE [HOOD]. Dissolve about 5 gr. of copper clippings in warm *aqua regia*, using the minimum of nitric acid that will effect the solution of the metal. Why is the nitric acid required, and what other substances might serve the same purpose? Evaporate to dryness on the steam bath [HOOD] and re-dissolve in 25 c.c. of water. Transfer to a flask, add an equal volume of concentrated hydrochloric acid and about 10 gr. of copper clippings and boil gently until the green color has vanished (?).

To a small part of this solution, when cold, add sodium hydroxide solution (?). Why is so much of this required? Divide the mixture into two parts. Notice whether the precipitate undergoes any change on shaking with air (?). For comparison, add sodium hydroxide solution to cupric sulphate solution (?). Explain. Heat the other half (?).

Pour the rest of the cuprous chloride solution into a large amount of water in a beaker (?). Expose some of the substance while covered with water to the sunlight (?). What properties of cuprous chloride have you observed?

2. DOUBLE SALTS.

a. Saturate 25 c.c. of water at 70° with powdered potassium sulphate (about 5 gr.). Calculate the weight of crystallized cupric sulphate which must be taken to get an equi-molecular proportion, and dissolve it in its own weight of hot water. Mix the two solu-

tions, taking care not to allow any undissolved fragments of either salt to get into the mixture, and set the result aside to crystallize (?). Examine the form of crystals and compare with those of blue vitriol. Keep them for use later.

b. To a little cupric sulphate solution add potassium cyanide solution till no further change occurs (?) [R]. Keep this solution

After applying to these two preparations the tests in 4, *c* and *d*, state the nature of the difference between the two bodies here examined.

3. EQUIVALENT OF COPPER [Quant.]. Weigh carefully a small rod of pure zinc. Place in a beaker an exactly known weight of crystallized cupric sulphate (about 2 gr.), and dissolve in distilled water. Put the zinc in this solution and allow them to remain in contact until the latter is completely decolorized. Remove the zinc, free it carefully from the brown deposit (?), and dry and weigh it. What weight of zinc has gone into solution? Calculate from the formula of the blue vitriol the weight of copper taken. Calculate the equivalent of copper ($H = 1$), using the value for the equivalent of the zinc found in Chap. VI, 3, or, if zinc was not employed then, assume it to be 32.4. Look up the specific heat of copper [R] and find its atomic weight from the equivalent observed.

What other atomic weights could be measured on this plan?

4. REACTIONS OF CUPRIC SALTS. Use diluted cupric sulphate solution. What is the color of cupric sulphate itself? To what is the color of the solution due?

a. Test the reaction of the solution with neutral litmus paper (?) and explain.

b. Add ammonium hydroxide till no further change occurs (?). This is used as a test for salts of copper.

c. Pass hydrogen sulphide gas through another portion.

Make a solution of part of the crystals in 2, *a*, and apply this test to it (?) and to a part of the solution from 2, *b* (?).

d. Same as *c*, using potassium ferrocyanide solution in place of hydrogen sulphide. Answer the question at the end of 2.

e. Add potassium iodide solution to a fresh portion (?). Filter, wash the precipitate (?), and add a drop of the filtrate to starch emulsion (?).

f. Make a borax bead and heat it with a minute particle of cupric oxide in the oxidizing (?) and in the reducing (?) flame. The latter requires patience

g. Try the match test (Chap. XVI, 14) with any copper compound,

h. Boil a little of a dilute sugar solution with a few drops of sulphuric acid for a minute or two. Add cupric sulphate solution and excess of sodium hydroxide solution and warm (cf. 1) [R].

5. REACTIONS OF SILVER SALTS.

a. Take some silver nitrate solution and add to it dilute hydrochloric acid till no further precipitation occurs. Filter and wash with water.

What effect does the skin have on silver nitrate?

b. Treat part of the precipitate with ammonium hydroxide (?). Then add dilute nitric acid to the solution (?).

c. Place the rest of the precipitate in a porcelain crucible, put on it a piece of granulated zinc, and fill up with dilute sulphuric acid. Stir from time to time (?). After an hour or two pour off the acid, take out any unchanged zinc, wash with water by decantation, add ammonium hydroxide, and filter. Find out whether there is any silver chloride in the filtrate (?). When the filter paper is dry, place the dark powder in a hollow on a stick of charcoal and melt it with the flame of the blast-lamp (?).

d. To a very little silver nitrate solution, add some potassium bichromate solution (?). Test the solutions before and after mixing, with neutral litmus paper (?).

CHAPTER XXI.

MAGNESIUM, ZINC, CADMIUM, MERCURY.

1. PROPERTIES OF MAGNESIUM COMPOUNDS.

a. Try whether magnesium chloride dissolves completely in water (?).

Heat some of the crystals strongly in a dry test-tube (?). Test the reaction towards litmus paper of the water which condenses in the tube (?), and remove the liquid from the sides of the tube with a piece of filter paper. Does the residue dissolve in water? Explain.

b. To some diluted magnesium sulphate solution add ammonium hydroxide (?). Explain the result according to the theory of ionization. Now mix with some ammonium hydroxide several times its volume of ammonium chloride solution (what effect will this have on the ionization of ammonium hydroxide?) and then add the mixture to a fresh portion of the magnesium sulphate solution (?). Explain. To this combination of three solutions add sodium phosphate solution (?) [R]. Write the equation and expiain the purpose for which each ingredient was used.

c. To a fresh portion of the diluted magnesium sulphate solution add ammonium carbonate solution and warm (?). What other metal ions are precipitated by the same reagent? Repeat, adding excess of ammonium chloride solution to the magnesium sulphate solution before using the carbonate (?). Try whether, with this modification, the salts of those other metals still behave like those of magnesium. If you had a salt of magnesium mixed with a salt of one of those other metals, how would you proceed so as to precipitate a compound of the alkaline earth metal first and one of magnesium afterwards? Explain the effect of the ammonium chloride as in *b.*

Add two drops of hydrochloric acid (why?) to about 250 c.c. of the city water, evaporate to small bulk, and test it for calcium and magnesium.

d. Pass hydrogen sulphide through some magnesium sulphate solution (?).

2. SALTS OF ZINC. Use diluted zinc sulphate solution.

a. Ionic equilibrium. Through a little zinc sulphate solution (reaction towards litmus?), pass hydrogen sulphide till the solution is saturated (?). Filter, test the reaction of the filtrate with litmus paper (?), and add ammonium hydroxide (?). The succession of hydrogen sulphide and ammonium hydroxide has the same effect as adding ammonium sulphide.

Take a larger amount of zinc sulphate solution and add sulphuric acid to it cautiously until a sample ceases to give any precipitate with hydrogen sulphide. Explain. Now add much solid sodium sulphate, stir, and test a part with hydrogen sulphide again. Explain. Write this equation so as to show that the action is reversible and that an equilibrium exists.

b. Pass hydrogen sulphide through some diluted zinc acetate solution until it is saturated, filter, and add ammonium hydroxide to the filtrate. Explain the difference in behavior as compared with the sulphate. Preserve the filter paper for use in *d.*

c. To zinc sulphate solution add caustic soda till no further change occurs (?). Explain [R].

d. Take a piece of filter paper from *a* or *b* with a very little zinc sulphide on it, roll it up, and twist the platinum wire tightly round it. Roast the whole in the Bunsen flame. Moisten the ash with cobalt chloride solution and heat again (?).

3. CADMIUM SALTS. To two samples of a diluted solution of any cadmium salt add (*a*) hydrogen sulphide gas (?), (*b*) sodium hydroxide solution in excess (?). Acidify the former with hydrochloric acid (?). How do the salts of this metal differ in behavior from those of zinc?

By what reactions could you distinguish between salts of magnesium, zinc, and cadmium?

4. Apply to the instructor for three unknown substances.

5. MERCUROUS NITRATE. Place about 10 gr. of mercury with 15 c.c. of diluted (1:1) nitric acid in a small beaker and let the action go on for an hour or two, or until fresh crystals cease to be formed. Pour away the liquid and dissolve the crystals in water to which a few drops of nitric acid have been added (why?). This solution, if ready, may be used in 6.

How could you make mercuric nitrate solution?

6. REACTIONS OF SALTS OF MERCURY. Use diluted portions

of mercurous nitrate solution and of a solution of any mercuric salt with the following reagents. Compare results in each case.

a. Dilute hydrochloric acid (?). Treat the precipitate, if there is any, with ammonium hydroxide (?) [R].

b. Hydrogen sulphide to saturation (?), then acidify (?).

c. Ammonium hydroxide (?) [R].

d. Sodium hydroxide (?) and boil (?).

e. Potassium iodide till there is no further change (?).

f. Stannous chloride till there is no further change (?).

g. Clean copper clippings (?). Ascertain experimentally whether any copper goes into solution (?).

How could you distinguish a solution of a mercurous and of a mercuric salt from salts of silver, bismuth, magnesium, zinc, and cadmium?

h. Heat any salt of mercury strongly in a narrow tube closed at one end (?).

CHAPTER XXII.

ALUMINIUM, TIN, LEAD.

1. ALUMINIUM,

a. Recall the effect of hydrocloric acid on aluminium (Chap. V, 1, *a*) (?). Try diluted nitric acid (?).

b. Heat a piece of aluminium wire with sodium hydroxide solution for some minutes (?). To ascertain whether anything has gone into solution, neutralize with dilute hydrochloric acid (?). Neutralize a sample of the caustic soda solution employed (?). If there is a precipitate in either case, test it by 3, *a.*

2. ALUM. Prepare warm saturated solutions of anhydrous aluminium sulphate and ammonium sulphate in approximately equi-molecular proportions, mix them, and set aside (?). Obtain some large crystals by hanging a thread in the solution. Notice the form of the crystals.

Ascertain by experiments selected from 3 whether a solution of this salt behaves, in respect to the aluminium which it contains, like a mixture of the constituent salts or like a different salt.

3. REACTIONS OF ALUMINIUM COMPOUNDS. Use a diluted aluminium sulphate solution.

a. Add sodium carbonate solution (?). Isolate the precipitate and find out whether it is a carbonate or not.

b. To another portion add colorless ammonium sulphide (?). Find out experimentally whether the precipitate is a sulphide or not.

c. To another portion add sodium hydroxide solution gradually (?). Filter, suspend part of the precipitate in water, and treat with more sodium hydroxide solution (?). What other hydroxide behaves like this? Treat another part similarly with hydrochloric acid (?). What peculiarities does this hydroxide show?

d. Wrap up part of the filter paper from *c*, twist the platinum wire tightly round it, char in the Bunsen flame, moisten with cobalt chloride solution, and heat again (?).

e. To some cochineal solution add any solution containing aluminium sulphate and then ammonium hydroxide (?).

4. HALIDES OF TIN.

a. Stannous chloride. Dissolve tin in warm concentrated hydrochloric acid. Let the action go on until the acid is nearly exhausted. Use the solution in 4, *b*, and 5. Proceed with 6, 8, and 9 till it is ready.

b. Stannic halide [HOOD]. To part of the solution from *a* add bromine until the color ceases to be destroyed and drive off the excess of bromine by warming (?). Use this liquid in 5.

5. REACTIONS OF STANNOUS AND STANNIC SALTS. Use a portion of each of the above solutions with each reagent.

a. Saturate (test ?) each solution with hydrogen sulphide (?). Neutralize with ammonium hydroxide and add yellow ammonium sulphide to each product (?). Acidify each resulting solution with hydrochloric acid (?).

b. Add mercuric chloride solution to fresh portions of each (?). Boil a portion of the stannic halide with a piece of tin for a minute or two and test with mercuric chloride solution again (?).

c. Add sodium hydroxide solution to each until no further change occurs (?). What peculiarity do these hydroxides exhibit?

6. SOLUTION TENSION AND ION CONCENTRATION. Suspend a rod of tin about 60 mm. long by a thread from one end, and hang it near the bottom of a wide test-tube or narrow cylinder. Pour in through the dropping funnel, which must reach the bottom of the cylinder, first diluted hydrochloric acid (1:3) and then diluted stannous chloride solution. Perform the operation with care, in such a way that the solutions do not mix and that the surface at which they meet is near the middle of the rod of tin. Place the arrangement where it will not be disturbed, and examine it from time to time (?). Explain [R].

7. Apply to the instructor for two unknown substances.

8. LEAD.

a. Dissolve 5 gr. of lead acetate in 60 c.c. of water, place in it several pieces of granulated zinc and let them remain for an hour or two. Preserve the solution and, after 9, devise a way of showing the presence of zinc, and see whether it works.

b. Wash some of the lead from *a* with distilled water until the washings show no reaction with hydrogen sulphide. Put it in a shallow dish, moisten it with ordinary water, and let it remain for several days. Then test the water from time to time with hydrogen sulphide (?).

9. REACTIONS OF LEAD SALTS. Use diluted lead nitrate solution.

a. Hydrogen sulphide (?).

b. Hydrochloric acid (?). Filter and add hydrogen sulphide to part of the filtrate (?). Explain. What other chlorides are more or less insoluble in water?

c. Potassium iodide solution (?). Boil the result, filter, and examine the filtrate (?).

d. Add sodium hydroxide gradually (?) and then in excess (?). Compare behavior with that of hydroxides of zinc, aluminium, and tin.

e. Potassium bichromate solution (?).

Does lead form any compounds in which it is tetravalent [R]?

Explain the action of minium on hydrochloric acid (Chap. VIII, 1, *a*).

CHAPTER XXIII.

CHROMIUM, MANGANESE.

1. CHROMIC OXIDE. Mix some potassium bichromate (15 gr.) thoroughly with one-fifth its weight of powdered sulphur and heat with the blast-lamp in a porcelain crucible for fifteen minutes. Grind up the resulting mass in a mortar with water, filter, wash the green residue (?), and dry it on a radiator.

Make a borax bead, dissolve a particle of chromic oxide in it, and note the effects of the oxidizing and reducing flames on it (?). All chromium compounds give the same result. If chromic sulphate had been used, what would have been the nature of the chemical action?

2. CHROMIC CHLORIDE. Mix the chromic oxide prepared in 1 with one-third its weight of powdered wood charcoal, make into a stiff paste with a little strong starch emulsion, and mold the mixture into little pellets of the size of peas. Cover these with charcoal powder and heat them strongly in a closed crucible. Place them in a piece of hard glass tubing and dry thoroughly by heating in a slow stream of dried carbon dioxide. Then connect with a chlorine apparatus and heat more strongly [Blast-lamp]. Conduct any superfluous chlorine into a test-tube filled with sodium hydroxide. Describe the substance which is formed and try its solubility in water and acids.

3. CHROME-ALUM. Dissolve 10 gr. potassium bichromate in water, add the amount of sulphuric acid necessary to form potassium sulphate and chromium sulphate, heat to boiling and add alcohol (2–3 c.c.) until the yellow color has entirely given place to green. Notice the odor (?). Set the solution aside to evaporate spontaneously. Examine the form and color of the crystals when they appear. What is the color of their solution in water?

4. **Chromates.** Melt 5 gr. potassium carbonate with equal amounts of potassium hydroxide and potassium nitrate at a low temperate in an iron crucible and stir in 5 gr. of powdered chromite. Heat strongly (blast-lamp) for several minutes (?). When the mass has cooled, dissolve it in water. Add dilute nitric acid until the solution is acid (?). Note the change in color (?).

5. **Chromic acid.** Make a cold saturated solution of sodium bichromate, add it to two volumes of concentrated sulphuric acid and cool (?). Filter through a plug of asbestos and dry on a tile.

6. Take some potassium bichromate solution and run into it potassium hydroxide from a burette till the change in color is complete. A test-tube trial will show the shade to be reached. Concentrate the solution and allow it to crystallize (?). What kind of salt is potassium bichromate ?

7. **Reactions of chromic salts.** Use diluted chrome-alum solution. What are the ions in the solution ?

a. Boil one portion of the solution for some time (?).

b. To another portion add sodium hydroxide solution at first a little (?), then excess (?). Boil (?).

c. Add ammonium sulphide (?). Is the precipitate a sulphide ?

d. Add excess of sodium hydroxide solution and then a large volume of bromine water, and heat (?). Try lead dioxide instead of bromine (?). Infer the nature of the action from the change in color.

8. **Reactions of chromates.** Use diluted potassium chromate solution. What are the ions in the solution ?

a. Recall the actions of hydrogen sulphide, of sulphur dioxide, and of hydrogen peroxide.

b. Add colorless ammonium sulphide and warm (?), then acidify (?).

c. Add lead nitrate and barium chloride to separate portions.

9. **Manganous and manganic salts.** Recall the preparation of a manganous salt in Chap. VIII, 1, *b*. Name a manganic salt. What are the colors of their solutions [R] ? The

chemical actions in 10 can be followed by noting the changes in color.

10. MANGANATES AND PERMANGANATES.

a. Fuse a mixture of 5 gr. potassium hydroxide, 2.5 gr. potassium chlorate, and 5 gr. finely powdered manganese dioxide at a red heat till effervescence ceases (?). Add the last ingredient gradually. Dissolve the mass in a small amount of water.

b. Dilute a part of the clear solution with a very large amount of water (?). If no change should occur, pass carbon dioxide into the diluted solution (?).

c. To a portion of the green solution add a few drops of alcohol and warm (?).

d. To the rest of the green solution add a boiling solution of oxalic acid (?).

e. Repeat *c* and *d* with potassium permanganate solution acidified by adding two drops of concentrated sulphuric acid (?)

f. Add acidified permanganate to ferrous ammonium sulphate solution till the pink color is permanent (?). To the product add ammonium hydroxide (?). What change has taken place in the iron (cf. Chap. XV, 4, *b*) ?

g. Recall the action of the same reagent on hydrogen sulphide (Chap. XIII, 3, *d*) and on sulphurous acid (Chap. XIII, 9, *d*).

11. Apply to instructor for two unknown substances.

12. REACTIONS OF MANGANOUS SALTS. Use any manganous salt.

a. Borax bead in oxidizing (?) and reducing (?) flames.

b. Bead of a mixture of sodium carbonate and sodium nitrate on a platinum wire with any manganese compound (?).

c. To a diluted solution of a manganous salt, add ammonium sulphide (?). Is the product a sulphide ?.

d. To another portion add sodium hydroxide (?). Divide into two parts. Shake one with air (?). To the other add bromine water and warm (?).

CHAPTER XXIV.

IRON, COBALT, NICKEL.

1. IRON. Recall the action of iron on dilute acids (Chap. V, 1, *a*, *b*, *c*), also its preparation from the oxide (Chap. V, 5, *a*)

2. IRON AMMONIUM ALUM [HOOD]. Weigh 3.5 gr. of concentrated sulphuric acid into an evaporating dish, add 20 gr. of crystallized ferrous sulphate, and dissolve in 25–30 c.c. of water. Heat on a square of wire gauze and add concentrated nitric acid drop by drop till the color of the solution, dark at first (?), changes to a light brown (? Chap. XV, 4, *b*). Evaporate to a syrup on the steam bath, dissolve the residue in the minimum amount of boiling water, add 3.5 gr. of ammonium sulphate, likewise dissolved in the minimum amount of boiling water, and set aside to crystallize. Describe the crystals. Collect them and wash them free from the mother liquor, dry with filter paper, and preserve for use in 4.

Chlorine, bromine, and other oxidizing agents have the same effect as the nitric acid here used.

3. SALTS OF COMPLEX ACIDS. Ferrocyanide and ferricyanide of posassium. Take some potassium ferrocyanide solution in a test-tube and add bromine water until a drop of the solution gives no blue precipitate with ferric chloride. What does the solution contain [R]?

4. REACTIONS OF FERROUS AND FERRIC SALTS.

a. Borax bead with any compound of iron in oxidizing and reducing flames (?).

Examine the action of the following substances on a diluted solution of ferrous ammonium sulphate (freshly prepared) and on a diluted solution of iron alum (made in 2) or ferric chloride.

b. To a portion of each solution add ammonium hydroxide (?). Note the effect on each precipitate of shaking with air (?).

c. To another pair of portions add ammonium sulphide solution (?) [R]. Is the precipitate soluble in hydrochloric acid? How could you prove experimentally that free sulphur is formed in the case of ferric salts?

d. Potassium ferrocyanide solution (?).

e. Potassium ferricyanide solution (?).

f. Potassium sulphocyanide solution (?).

g. The reduction of ferric salts to ferrous salts in solution is as easy as the converse operation (Chap XIII, 3, *e*). Boil a little diluted ferric chloride solution with a pinch of powdered iron and test a drop from time to time (?). What reagent will you use in testing?

h. Ascertain experimentally whether solutions of ferro- and ferricyanides contain a detectable proportion of iron ions.

i. Show that the crude hydrochloric acid contains ferric chloride (?). Show that the same substance contains sulphuric acid as another impurity.

5. REACTIONS OF SALTS OF COBALT. Use diluted cobalt chloride solution.

a. Borax bead in oxidizing and reducing flames (?).

b. Add sodium hydroxide solution — first a little (?), then excess, and warm (?).

c. Ammonium sulphide solution (?).

6. REACTIONS OF SALTS OF NICKEL. Use diluted nickel sulphate solution.

a, b, c. Same as in 5.

7. Obtain two unknown substances from the instructor and identify them.

APPENDIX

TENSION OF AQUEOUS VAPOR IN MILLIMETERS

TEMP.	PRESS.	TEMP.	PRESS.	TEMP.	PRESS.
0°	4.6	16°	13.5	26	25.1
5	6.5	17	14.4	27	26.5
8	8.0	18	15.4	28	28.1
9	8.6	19	16.3	29	29.8
10	9.2	20	17.4	30	31.5
11	9.8	21	18.5	31	33.4
12	10.5	22	19.7	32	35.4
13	11.2	23	20.9	33	37.4
14	11.9	24	22.2	34	39.6
15	12.7	25	23.6	100	760.0

DEGREE OF IONIZATION OF ACIDS, BASES AND SALTS.

Except where otherwise specified, the figures give the percentage ionized in a normal solution at 18°, calculated from the electrical conductivities.

ACIDS	PER CENT.	SALTS	PER CENT.	BASES	PER CENT
HCl	78	KCl	75	LiOH	63
HCl (conc., 35%)	13.6	NH_4Cl	74	NaOH	73
HNO_3	82	KNO_3	64	KOH	77
HNO_3 (conc., 62%)	9.6	K_2SO_4	53	$Ba(OH)_2$	69
H_2SO_4	51	Na_2HPO_4(N/32)	83	$Ca(OH)_2$ (N/64, 25°)	90
H_2SO_4 (conc., 95%)	.7	$KC_2H_3O_2$	64	$Sr(OH)_2$ (N/64, 25°)	93
$H.H_2PO_4$(N/2, 25°)	17	K_2CO_3	(49)	$Ba(OH)_2$ (N/64, 25°)	92
$HC_2H_3O_2$	.37	$ZnSO_4$	24	NH_4OH	.37
$H.HCO_3$ (N/25)	.21	$CaSO_4$ (N/100)	63	H_2O	< 1 per mil.

SELECTION FOR STUDENTS WITH ADMISSION CREDIT IN CHEMISTRY

Chap.
I, 1; 2; 3; 5; 6.
III, 1, *b*; 2, *a* or *b*.
IV, 2, parenthesis; 4; 5; 6 (?); 7.
V, 1; 2, *c*, *d*; 5.
VI, 1; 2; 3, *a*; 4; 5.
VII, 2; 3, *d*; 6; 7.
VIII, 1, *a*, *c*; 3; 4, *a*, *b*, *c*.
IX, 1, *b*; 2; 4, *d*.
X, 1; 2, *a*, *c*, *d*; 3; 4; 5; 6.
XI, 1; 2, *d*, *e*; 4; 6; 7; 8,
XII, 1, *b*; 2, *a*; 4.
XIII, 1, *d*, *e*; 2, *c*; 3; 4, *g*; 5, *c*; 9; 10; 11; 12.

Chap.
XIV, 2, *b*; 5, *b*.
XV, 1, *b*, *d*; 2; 3, *b*, *c*; 4; 5.
XVI, 2; 3, *b*; 5; 6, *b*; 8; 9; 12; 13.
XVII, 1; 3.
XVIII, 2; 3; 4; 6; 7; 8; 9.
XIX, 3; 4; 5; 7.
XX, 1; 2.
XXI, 1; 2; 3; 4; 5; 6.
XXII, 1; 2; 4; 6; 8.
XXIII, 1; 2; 4; 5; 10.
XXIV, 3.

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